U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-299 351

Refinery Waste Disposal Screening Study

Radian Corp, McLean, VA

Prepared for

Environmental Protection Agency, Research Triangle Park, NC

Jun 79

PB 299351

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-79-019
June 1979

Air

EPA

Refinery Waste Disposal Screening Study

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-450/3-79-019

2.

3. RECIPIENT'S ACCESSION NO.
PB299351

4. TITLE AND SUBTITLE
Refinery Waste Disposal Screening Study

5. REPORT DATE
May 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Juanita Galloway

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Radian Corporation
Suite 125, Culpeper Building
7923 Jones Branch Drive
McLean, Virginia 22102

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-2608, Task 61

12. SPONSORING AGENCY NAME AND ADDRESS
Office of Air Quality Planning Standards
U.S. Environmental Protection Agency
Emission Standards and Engineering Division
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA 200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Published data and data supplied to the OAQPS in response to a 1978 request for information were used to estimate the quantity and phase characteristics of major refinery solid waste streams. A supplementary sampling program was described which will provide a data base for development of an AP-42 factor for VOC emissions from refinery solid wastes. Solid waste control technologies utilized by the refining industry were analyzed and described. A listing was developed of operators involved in the organic waste industry.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Refinery Waste Waste Disposal		

18. DISTRIBUTION STATEMENT
Unlimited

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
188

22. PRICE
PCA09 / MF A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/3-79-019

Refinery Waste Disposal Screening Study

by

Ms. Juanita Galloway

Radian Corporation
Suite 125, Culpeper Building
7923 Jones Branch Drive
McLean, Virginia 22102

Contract No. 68-02-2608
Project No. 61

EPA Project Officer: Kerri C. Brothers

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

June 1979

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or for a nominal fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by the Radian Corporation, Suite 125, Culpeper Building, 7923 Jones Branch Drive, McLean, Virginia 22102, in fulfillment of Contract No. 68-02-2608. The contents of this report are reproduced herein as received from the Radian Corporation. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-450/3-79-019

TABLE OF CONTENTS

Page

List of Figures ... iv
List of Tables ... v

1.0 INTRODUCTION ... 1
  1.1 Approach ... 1
    1.1.1 Quantify and Characterize Waste ... 1
    1.1.2 Waste Control Technology ... 2
    1.1.3 Listing of Solid Waste Operations ... 2
  1.2 Summary of Results ... 3

2.0 CONCLUSIONS AND RECOMMENDATIONS ... 5
  2.1 Conclusions ... 5
  2.2 Recommendations ... 5

3.0 SOLID WASTE GENERATION ... 6
  3.1 Data Collection ... 6
  3.2 Data Compilation ... 6
  3.3 Data Analysis ... 13
  3.4 Comparison with Previous Studies ... 18
  3.5 Extrapolation of Data ... 21

4.0 HYDROCARBON EMISSIONS ... 25
  4.1 Data Analysis ... 25
    4.1.1 Phase Composition of Waste Streams. 25
    4.1.2 Hydrocarbon Content of Refinery Solid Waste ... 25
    4.1.3 Estimation of VOC Emissions ... 28
  4.2 Data Limitations ... 30
  4.3 Factors Controlling Volatile Emissions ... 30
  4.4 Supplementary Data Collection Program ... 34
  4.5 VOC Emissions from Other Sources ... 35

5.0 SOLID WASTE MANAGEMENT PRACTICES ... 37
  5.1 Source Control ... 37
  5.2 Treatment ... 38
  5.3 Final Disposal ... 39
  5.4 Process Descriptions ... 41

Bibliography ... 43

TABLE OF CONTENTS (Continued)

		Page
Appendix I	Evaluation of Solid Waste Processing and Disposal Techniques	I-1
Appendix II	Description of Refinery Solid Waste Streams	II-1
Appendix III	Estimation of the Parameters of the Log-normal Distribution	III-1
Appendix IV	Selection of Refineries for Supplementary Sampling Program	IV-1
Appendix V	Supplementary Sampling Program	V-1

LIST OF FIGURES

Number Page

3-1 Histogram of Solid Waste Generation Data for API Separator 14

3-2 Histogram of the Logarithms of Solid Waste Generation Data for API Separator Sludge 16

4-1 Organic Emission Versus Volatility of Hydrocarbon Phase 29

5-1 Matrix Summary of Control Technologies and Refinery Waste Streams 42

Appendix IV-1

1 Block Flow Diagram for a Representative U.S. Refinery IV-3

LIST OF TABLES

Number | Page

3-1 Companies Receiving EPA-QAQPS Data Request Forms and Refineries for Which Forms were to be Completed 7
3-2 Solid Waste Streams Included in the EPA-OAQPS Survey 9
3-3 Solid Waste Generation Data 12
3-4 Solid Waste Generation Factors 17
3-5 Comparison of Jacobs and EPA-OAQPS Generation Factors 20
3-6 Comparison of API and EPA-OAQPS Generation Factors 22
3-7 Annual Solid Waste Generation of the Entire U.S. Petroleum Refining Industry 23
4-1 EPA-OAQPS Survey Summary of Reported Phase Data Water, Solid, and Hydrocarbon Content of Refinery Solid Waste Streams 26
4-2 EPA-OAQPS Survey Total Hydorcarbons in Refinery Solid Wastes 27
4-3 Volatile Components of Waste Streams in EPA-OAQPS Survey 31
4-4 Factors Affecting VOE From Solid Wastes 33

Appendix IV

1 Comparison of "Representative" Refinery Product Slate with Total Actual U.S. Production IV-4
2 Refinery Process Unit Capacities "Representative" Compared to Average of U.S. Refineries IV-5
3 Subcategorization of the Petroleum Refining Industry Reflecting Significant Differences in Wastewater Characteristics IV-8
4 Refineries Simulated by Cluster Models IV-11
5 PAD Districts and Bureau of Mines Refining Districts IV-12
6 Summary of Major Refinery Processing Units for 1973 ..... IV-14

LIST OF TABLES (Continued)

Number		Page
Appendix V		
1	Solid Waste Streams Number of Samples and Phases to be Analyzed	V-2
2	Refinery Solid Waste Constituents to be Analyzed	V-3
3	Refinery Solid Waste Stream Analyses Currently Used Methods and Costs	V-4
4	Solid Waste Sampling and Analysis Comparison: Precision Versus Cost	V-6

1.0 INTRODUCTION

The Emission Standards and Engineering Division of EPA's Office of Air Quality Planning and Standards (OAQPS) is currently investigating the need to control volatile organic carbon (VOC) emissions from the handling and disposal of wastes from the U.S. Petroleum Refining Industry. Radian Corporation was contracted to assist OAQPS in determining the quantities, characteristics, and fate of solid wastes produced by the refining industry and to estimate the national VOC atmospheric emissions resulting from refinery solid waste treatment and disposal. As defined by this program, solid wastes include all refinery waste streams which are not controlled by existing wastewater and air emissions regulations.

Radian's objectives in this program were as follows:

- Estimate the quantity and characteristics of major refinery solid waste streams.
- Compare AP-42 emission factors against the refinery solid waste data base to determine if the data base warranted revisions to the AP-42 factors.
- Describe and evaluate both proven and potential solid waste control technologies utilizable by the refining industry.
- Develop a comprehensive listing of operators involved in the organic wastes industry.

1.1 Approach

1.1.1 Quantify and Characterize Wastes

Data submitted to the OAQPS by eight petroleum refining companies, in response to an April 1978 request served as the primary data base for this study. The industry responses were screened for obvious errors, keypunched and validated. They were filed on an automated data base on the Statistical Analyses System to facilitate computation. Statistical models were built for the solid waste streams generation rates and the most precise estimate of the mean generation rates. Using the models, estimates of the national waste generation factors and confidence intervals for the estimates were determined.

1.1.2 Waste Control Technology

Existing and planned techniques used by the refining industry were identified and described. Identification of these processes required a survey of the literature, contacts with industry representatives, and review of industry responses to the 1978 EPA survey of eight refining companies. The technology search covered methods used for recovery, treatment, and disposal of refinery solid wastes.

After the solid waste technologies were identified, advantages and disadvantages of each technique were defined in Appendix I. The discussion of each technology covered the following areas:

- Development status
- Performance
- Secondary pollutants
- Cost and energy requirements

1.1.3 Listing of Solid Waste Operations

A listing was developed of names, addresses and telephone numbers of operators involved in the collection, disposal, treatment and reclamation of organic wastes. These firms accepted wastes from petroleum refineries, re-refiners, waste solvent reclaimers, chemical processing plants and degreasing operations.

The list was compiled through use of recent EPA surveys, contracts with refinery management, state and local agencies, representatives from the disposal industry, and trade associations. The search focused on geographical areas where the refining industry is most concentrated. The list was submitted as a separate report during the course of this study.

1.2 Summary of Results

The major finding of this study was that volatile organic emissions resulting from handling of refinery solid wastes could not be accurately estimated from the available data. However, it can be estimated from the OAQPS data base that the total hydrocarbon content of solid waste streams from United States refineries is approximately 190,000 tons/year (dry weight). About 75 percent of the hydrocarbons in the solid wastes are contained in four waste streams: Dissolved Air Floatation Skimmings, Slop Oil Emulsion Solids, API Separator Sludge, and Biosludge.

The release of hydrocarbons from the solid wastes is primarily dependent on volatility. For example, if as much as 10 percent of the total hydrocarbon content were volatile, emissions from refinery solid waste could approach 19,000 tons/yr. It may be expected that solid waste hydrocarbon volatility would be low, due to degradation or loss of volatiles in upstream refining process units and wastewater treatment facilities.

Data on hydrocarbon volatility and on many other factors which may affect VOC emissions from solid wastes were not obtained in the present study. Radian did, however, identify and describe the data gaps and develop a data collection program that would provide adequate information to estimate VOC emissions. A better characterization of refinery solid wastes would also aid the design of treatment, disposal, and resource recovery systems, and could identify sources of hazardous compounds. A detailed discussion of this data collection system is provided in the Appendices.

During the conduct of this study, Radian determined that in addition to the petroleum refining industry, other industries could contribute significant quantities of solid organic wastes. These industries include: petroleum re-refiners, solvent reclamation, and degreasing. It was recommended that these industries be included in a comprehensive assessment of organic solid waste and VOC emissions from the waste streams.

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 Conclusions

1. The solid waste generation data collected in the EPA-OAQPS survey are an adequate basis for only order-of-magnitude estimates of solid waste generation by the petroleum refining industry.

2. The existing data on the volatile organic carbon content of refinery solid waste is not adequate for accurately estimating the volatile emissions from the solid waste during processing and disposal.

3. Industries other than the petroleum refining industry generate solid wastes that contain significant amounts of volatile organic carbons which could be emitted during solid waste processing and disposal.

2.2 Recommendations

1. A well-designed sampling program to obtain the data required to develop accurate estimates of refinery solid waste generation and the volatile emissions from that solid waste should be initiated.

2. Studies of the volatile emissions from solid waste generated by industries other than the petroleum refining industry should be initiated.

3.0 SOLID WASTE GENERATION

Estimates of the quantities of solid waste generated by the petroleum refining industry are needed as a basis for estimating the atmospheric emissions from refinery solid waste handling and disposal. EPA-OAQPS recently conducted a survey in which one of the major objectives was to collect solid waste generation rate data. The collection, compilation, and analysis of this data are described in this section. The resulting solid waste generation factors are compared to generation factors developed in previous studies. The generation factors are then used to estimate annual solid waste generation by the petroleum refining industry.

3.1 Data Collection

In April 1978, EPA-OAQPS initiated a survey to gather information needed to quantify the atmospheric emissions from refinery solid waste handling and disposal. Data request forms were mailed to the companies listed in Table 3-1 with instructions to complete one form for each refinery listed under the company name in the table. The data request form contained twenty waste streams for which quantity, composition, frequency of generation, storage, transport, and disposal information was sought. The twenty waste streams of interest are listed in Table 3-2. A description of most of the waste streams is provided in Appendix I. Satisfactory responses were received from all of the companies by September 1978.

3.2 Data Compilation

The solid waste generation rate data were read from the survey forms and recorded by waste stream. During the compilation process, it was found that a substantial amount of double accounting was occurring. The double accounting resulted from the

TABLE 3-1

COMPANIES RECEIVING EPA-OAQPS DATA REQUEST FORMS AND REFINERIES FOR WHICH FORMS WERE TO BE COMPLETED

Company and Refinery	Refinery Number
Ashland Petroleum Company (ASH)	
Catlettsburg, KY	1
Canton, OH	2
Buffalo, NY	3
St. Paul, MN	4
Continental Oil Company (CONT)	
Lake Charles, LA	5
Ponca City, OK	6
Billings, MT	7
Getty Refining & Marketing Company (GETT)	
El Dorado, KS	8
Delaware City, DE	9
Marathon Oil Company (MARA)	
Texas City, TX	10
Detroit, MI	11
Robinson, IL	12
Garyville, LA	13
Mobil Oil Corporation (MOB)	
Paulsboro, NJ	14
Ferndale, WA	15
Joliet, IL	16
Beaumont, TX	17
Augusta, KS	18
Buffalo, NY	19
Torrance, CA	20
Phillips Petroleum Company (PHILL)	
Kansas City, KS	21
Borger, TX	22
Sweeney, TX	23

TABLE 3-1

COMPANIES RECEIVING EPA-OAQPS DATA REQUEST FORMS AND REFINERIES FOR WHICH FORMS WERE TO BE COMPLETED (Continued)

Company and Refinery	Refinery Number
Texaco Inc. (TEX)	
Lockport, IL	24
Lawrenceville, IL	25
Westville, NJ	26
Anacortes, WA	27
Port Arthur, TX	28
St. James Parish, LA	29
Wilmington, CA	30
Union Oil Company (UNION)	
Beaumont, TX	31
Chicago, IL	32
Los Angeles, CA	33
Rodeo, CA	34

TABLE 3-2

SOLID WASTE STREAMS INCLUDED IN THE EPA-OAQPS SURVEY

Stream	Stream Number
Slop Oil Emulsion Solids	1
Silt from Storm Water Runoff	2
Exchanger Bundle Cleaning Sludge	3
API Separator Sludge	4
Nonleaded Gasoline Tank Bottoms	5
Crude Tank Bottoms	6
Other Storage Tank Bottoms	7
Leaded Gasoline Tank Bottoms	8
Dissolved Air Flotation Skimmings	9
Kerosene Filter Clays	10
Other Filter Clays	11
HF Alkylation Sludge	12
Waste Bio-Sludge	13
Once-Through Cooling Water Sludge	14
FCC Catalyst	15
Coke Fines	16
Spent Amines	17
Salts from Regeneration	18
Ship and Barge Ballast	19
Other	20

reporting of generation rate data for waste streams that were subsequently discharged to the sewer system. To illustrate, suppose a refinery reported generating exchanger bundle cleaning sludge. The generation rate reported would be recorded under the exchanger bundle cleaning sludge waste stream. Also, suppose that this sludge was discharged to the sewer system. As a result, exchanger bundle cleaning sludge would appear in the wastewater treatment sludges; thus, the generation rate for exchanger bundle cleaning sludge would also be included in the generation rate reported for the wastewater treatment sludge waste streams.

An apparent solution to the double accounting problem was to continue to record the generation rates of all waste streams at the point of generation and then to subtract the generation rates of those waste streams discharged to the sewer system from the reported generation rates of the wastewater treatment sludges. Unfortunately, this approach was not feasible because the fate of a waste stream after it enters a sewer system cannot be determined. For example, discharging exchanger bundle cleaning sludge to a refinery sewer system could result in the sludge reacting with other wastes, being removed from the wastewater in any or all of several wastewater treatment units, and/or passing through the treatment process. As a result, the generation rate of a waste stream that is discharged to the sewer system could not be subtracted from the generation rates of wastewater treatment sludges because the disposition of the stream among the sludges was not known.

Another solution to the double accounting problem was to record the generation rates of those waste streams discharged to the sewer system as zero at their point of generation. The disadvantage of this approach is that the true generation rates for the waste streams that are discharged to the sewer system would be under-estimated. Under-estimation of the true generation rate of certain waste streams was considered to be preferable to over-estimation of the total solid waste generation rate for all the waste streams; therefore, this approach to eliminating double accounting was used.

The resulting compilation of solid waste generation rates by waste stream for all of the refineries surveyed was converted to a dry weight basis and then to a unit capacity basis. In order to convert the data to a dry weight basis, the composition data from the survey on moisture content of the waste streams was compiled. In some cases, data on moisutre content were not reported where generation rate data had been reported. The only other available source of refinery solid waste stream moisture content at the time of this analysis was a study done by Jacobs Engineering Company (JA-216); therefore, the moisture contents contained in this report were used where moisture data from the survey were missing.

Since some refineries in the OAQPS survey did not provide adequate capacity data, all capacities used in the solid waste calculations were obtained from the 1977 Annual Refining Survey published in the Oil and Gas Journal (CA-673). Capacities on a Barrels Per Calendar Day (BPCD) basis, reflecting actual volume of oil processed, were used to calculate the most accurate solid waste generation factors. Then, to permit direct comparison of the OAQPS data with the API and Jacobs Engineering studies, all calculations performed on a BPCD basis were converted to a Barrels Per Stream Day basis (BPCD = 0.9 x BPSD). The resulting solid waste generation rate data are presented by solid waste stream and refinery in Table 3-3.

Three potential biases in the survey were identified as a result of studying the data during the compilation process. First, the twenty waste streams were not adequately described.

TABLE 3-3

SOLID WASTE GENERATION DATA

(Dry Weight)

Metric Tons/Yr. / 1000 Barrels/Stream Day

Company (See Table 3-1)	Refinery No. (See Table 3-1)	Stream Number (See Table 3-2)																			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
ASH	1	0.52	(2)	(2)	4.55	0.01	0.01	0.05	0.01	0.43	0	0.45	0	0.17	0	5.95	0.02	(2)	0	0	0.09
ASH	2	0.58	(2)	(2)	2.26	0.01	0.01	0	0.01	0.46	0	0	5.44	0.11	0	2.09	0.02	(2)	0	0	0.08
ASH	3	0.60	(2)	(2)	2.56	0.01	0.01	0	0.01	3.55	0.35	0	0	0	0	4.02	0.02	(2)	0	(2)	0.17
ASH	4	0.31	1.29	(2)	0.13	0.01	0	0	0.01	0	0	0	6.09	UK	0	4.65	0.02	(2)	0	0	0
CONT	5	3.13	0	UK	0.37	UK	(2)	(2)	UK	0.81	0	0	0	2.19	0	0	6.35	UK	UK	UK	UK
CONT	6	0.58	4.52	UK	0.48	(2)	1.24	(2)	1.35	0	1.22	0	0.23	0	0	0.74	UK	(2)	0	0	3.86
CONT	7	UK	UK	(2)	0.21	0	0	0	0	0.64	0	0	0.79	4.61	0	1.94	0	(2)	0	0	0
GET	8	(2)	21.44	(2)	12.90	0.22	0	0.22	0.28	49.58	0	1.04	(2)	9.32	0	0.02	12.56	(2)	0	0	NR
GETT	9	NR	NR	NR	0.03	0.66	4.22	3.95	NR	0.51	NR	0.02	NR	10.80	NR	3.63	NR	NR	NR	NR	NR
MARA	10	3.24	0	0.51	2.54	(2)	0.05	(2)	0.04	14.09	0	0.05	7.60	7.66	0	4.05	0	0	(2)	(2)	(2)
MARA	11	NR	(2)	(2)	1.25	(2)	1.66	5.17	0.25	1.46	NR	0.14	NR	NR	0.04	NR	NR	(2)	NR	NR	NR
MARA	12	0.28	4.26	0.02	0.65	(2)	0	(2)	0.45	0.69	0.25	0	0	11.08	0	3.18	1.62	(2)	(2)	(2)	(2)
MARA	13	4.20	0	0.01	6.72	0.08	0.39	0.19	0	1.14	0	0	0	0	0	0	0	0	0	0.19	0
MOB	14	(1)	UK	(2)	5.56	UK	(2)	(2)	0.04	37.36	0.17	0	0.24	7.64	0	0	UK	(2)	(2)	(1)	(2)
MOB	15	UK	UK	0.02	0.95	(2)	UK	(2)	0.01	UK	0	0.01	0	19.64	0	0	0	(2)	(2)	UK	NR
MOB	16	0.03	2.25	(2)	0.59	0	0	(2)	0	0.18	0	0	0.64	0.03	0	4.50	UK	0	0	0	NR
MOB	17	UK	UK	UK	UK	UK	UK	UK	UK	18.70	0.05	0	0	(2)	0	1.18	UK	0	UK	UK	UK
MOB	18	2.16	1.09	0.01	0.36	UK	0.18	0.36	1.44	0	0.17	0	(2)	0	0	0	0	(2)	0	0	0
MOB	19	(1)	NR	NR	2.12	(2)	0.91	(2)	0.31	3.09	0.81	0	0	0	1.85	8.37	0	NR	0	UK	0
MOB	20	(1)	0	0	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	0	0	(1)	UK	0	0	0	(1)
PHILL	21	UK	2.45	UK	27.72	UK	0.07	0	UK	6.20	0	29.70	(2)	0.19	0	4.30	0	0	0	0	UK
PHILL	22	0	1.35	(2)	0.66	UK	0	UK	UK	11.61	0	0	1.30	0.34	0	34.92	0	UK	UK	0	(2)
PHILL	23	(1)	UK	UK	55.92	UK	UK	UK	UK	14.64	0	0.05	0.03	UK	0	14.28	UK	UK	UK	UK	NR
TEX	24	0.19	12.96	(2)	59.34	(2)	0	9.16	0.01	67.09	0.19	0	0	1.24	0.56	9.25	2.19	0	0	0	NR
TEX	25	(2)	NR	(2)	(2)	(2)	(2)	(2)	(2)	NR	(2)	NR	NR	(2)	NR	(2)	NR	(2)	NR	NR	(2)
TEX	26	0	0	NR	0.32	(2)	4.09	0.51	0.03	0	0.04	0.01	0	0.51	0	1.23	0	0	(2)	(2)	(2)
TEX	27	9.32	NR	NR	NR	(2)	3.00	(2)	0.58	0	0.06	0	0	NR	4.04	(2)	0	NR	(2)	(2)	NR
TEX	28	0	UK	UK	(2)	0.01	0.10	0.51	0.18	0	0.56	27.77	0	(2)	UK	0	0	0	(2)	(2)	(2)
TEX	29	0.09	0.09	0	0.25	UK	UK	0.10	0.10	0	0.30	0	0	1.97	0	(2)	0	0	(2)	0.77	(2)
TEX	30	UK	0.05	UK	0.45	UK	UK	UK	UK	0.70	0	0	0	0	0	5.16	UK	0	UK	NR	0.29
UNION	31	UK	UK	UK	0.21	0	(2)	(2)	(2)	0	0	12.37	0	11.25	0	6.75	0	(2)	(2)	(2)	0
UNION	32	0	9.97	UK	1.67	UK	0.13	UK	UK	0	0	0.47	0	9.54	0	3.87	UK	UK	UK	UK	0.09
UNION	33	23.43	0.02	0.01	6.22	UK	0.04	(2)	UK	1.38	0	0.28	0	0	0.17	8.00	0	0.01	NR	12.83	(2)
UNION	34	0.03	1.3	0.17	1.6	0.02	0.07	0.03	0.1	1.7	0	0.03	0	0.76	0.9	0	7.6	0	0	(2)	0.07

---

1 - Reported in barrels/year.

2 - Waste stream discharged to sewer system. To avoid double accounting, quantity of waste stream was considered to be zero.

Key

UK - Unknown

NR - Not reported

As a result, there appeared to be a lack of uniformity in the interpretation of the nomenclature used to describe the waste streams which probably caused certain quantities of solid waste to be attributed to the wrong waste streams. Second, the allowance of best estimates in the absence of actual measurements was apparently used by many respondents as authority to provide estimates which were not based on any sampling. Third, most likely a completely random or a stratified random sample was not made. A bias can result if a random selection of companies and refineries within each company is not made. These biases could be a source of error in the estimates of the mean solid waste generation rates for all refineries.

3.3 Data Analysis

The solid waste generation rate data in Table 3-3 was examined to identify any generation rates which seemed unreasonable based on knowledge of typical refinery operations. The generation rate of 12.56 metric tons/year per 1000 barrels/stream day (MTPY/TBPSD) reported by Refinery 8 for Stream 16 was considered unreasonably large, and the 0.02 MTPY/TBPSD rate reported by Refinery 8 for Stream 15 was considered unreasonably low. As a result, these two generation rates were eliminated from the data base.

The remaining generation rate data in Table 3-3 were keypunched, verified, and placed in a data file. A histogram of the generation rate data for each waste stream was developed. As is the case with much process and environmental data, the histograms revealed that the data are skewed. A typical example is contained in Figure 3-1. This is a histogram of the number of

FIGURE 3-1

HISTOGRAM OF SOLID WASTE GENERATION RATE DATA FOR API SEPARATOR

Generation Rate (Dry weight)
(Metric tons/yr. per 1000
barrels/stream day)

```
                                                                                                    CUM.              CUM.
                                                                                            FREQ.   FREQ.   PERCENT   PERCENT
  0-33  ********************************************************************************    16      16      55.17     55.17
   3-6  *************************                                                            5      21      17.24     72.41
   6-9  ********************                                                                 4      25      13.79     86.21
 12-15  *****                                                                                1      26       3.45     89.66
 27-30  *****                                                                                1      27       3.45     93.10
 30-33  **********                                                                           2      29       6.90    100.00
        ----+----+----+----+----+----+----+----+----+----+----+----+----+----+----+----+
            1    2    3    4    5    6    7    8    9   10   11   12   13   14   15   16
```

NUMBER OF REFINERIES WHOSE GENERATION RATE
FALLS IN THE INTERVAL

refineries reporting various generation rates for API Separator Sludge. To illustrate, sixteen refineries reported generation rates between 0 and 3 MTPY/TBPSD, five refineries reported 3-6 MTPY/TBPSD, four refineries reported 6-9 MTPY/TBPSD, one refinery reported 12-15 MTPY/TBPSD, one refinery reported 27-30 MTPY/TBPSD, and two refineries reported 30-33 MTPY/TBPSD.

As can be seen, several large generation rates have been reported relative to the bulk of the data. For this type of data, the arithmetic average is an inefficient estimation of the population average. The median, although being insensitive to a few large values, is also inappropriate as an estimate of the population mean. Since the data are not symmetric, the population mean and median are different. The sample median is an under-estimate of the population mean. For example, the mean for the API separator sludge is 6.8 MTPY/TBPSD while the median is 0.96 MTPY/TBPSD.

In order to efficiently estimate the population mean, a lognormal model was fit to the non-zero generation rate data for each waste stream. This model is appropriate when the natural logarithms of the data are approximately normally distributed. The percentage of non-generating refineries was modeled by a binomial distribution. Figure 3-2 is a histogram of the logs of the API separator sludge data. The most efficient unbiased estimates of the population mean and variance have been given by Finney (FI-163). These estimators have been used in computing an estimate of the population mean or the generation factor for each waste stream. The mathematical details about the lognormal distribution and the estimates are contained in Appendix II. The generation factors computed using the estimate of the population mean for the lognormal model are presented in the first column of Table 3-4. A generation factor is not shown for Stream 18 because no non-zero generation rates were reported for this stream.

FIGURE 3-2

HISTOGRAM OF THE LOGARITHMS OF SOLID WASTE GENERATION RATE DATA FOR API SEPARATOR SLUDGE

```
  Log (Generation Rate)
(Metric tons/year per 1000 barrels/stream day)

                                                              CUM.                 CUM.
                                                       FREQ.  FREQ.   PERCENT   PERCENT
 -3.5  |**********                                       1      1       3.45      3.45
 -2.0  |**********                                       1      2       3.45      6.90
 -1.5  |******************************                   3      5      10.34     17.24
 -1.0  |****************************************         4      9      13.79     31.03
 -0.5  |****************************************         4     13      13.79     44.83
  0.0  |******************************                   3     16      10.34     55.17
  0.5  |**********                                       1     17       3.45     58.62
  1.0  |****************************************         4     21      13.79     72.41
  1.5  |********************                             2     23       6.90     79.31
  2.0  |********************                             2     25       6.90     86.21
  2.5  |**********                                       1     26       3.45     89.66
  3.5  |**********                                       1     27       3.45     93.10
  4.0  |********************                             2     29       6.90    100.00
       ----------+----------+----------+----------+
                 1          2          3          4
                   Number of Refineries
```

TABLE 3-4

SOLID WASTE GENERATION FACTORS
(Dry Weight)

Waste Stream (See Table 3-2)	Generation Factor for Generating Refineries Metric tons/year 1000 barrels/stream day	Estimate of Percentage of Generating Refineries	95% Confidence Interval on Estimate of Percentage of Generating Refineries	Generation Factor for All Refineries Metric tons/year 1000 barrels/stream day	95% Confidence Interval for Generation Factor for All Refineries Metric tons/year 1000 barrels/stream day
1	4.44	76	58 - 89	3.37	0.55 - 16.3
2	12.8	62	43 - 78	7.94	0.93 - 52.4
3	0.083	47	29 - 65	0,039	0.005 - 0.21
4	3.19	91	76 - 98	2.90	1.22 - 5.34
5	0.083	62	43 - 78	0.051	0.0045 - 4.1
6	1.21	68	49 - 83	0.82	0.14 - 3.2
7	2.43	50	32 - 68	1.22	0.013 - 8.5
8	0.30	82	65 - 93	0.25	0.061 - 0.79
9	6.09	71	52 - 85	4.32	1.4 - 9.9
10	0.36	38	22 - 56	0.14	0.031 - 0.46
11	5.8	44	27 - 62	2.55	0.24 - 21.5
12	6.7	29	15 - 47	1.94	0.12 - 23.9
13	8.95	62	43 - 78	5.55	1.27 - 20.5
14	0.67	21	8 - 38	0.14	0 - 2.7
15	8.3	68	49 - 83	5.64	2.1 - 7.0
16	4.05	50	32 - 68	2.03	0.09 - 46.3
17	0.006	15	4 - 31	0.001	0 - 0.02
18	-----	--	-------	----	-----
19	3.96	29	15 - 47	1.15	0 - 59,600
20	0.42	32	17 - 51	0.13	0.008 - 1.32

An estimate of the population mean for each waste stream including not only the refineries reporting non-zero generation rates but also the refineries reporting zero generation rates was desired; therefore, the non-generating refineries had to be taken into account. The percentage of generating refineries in the total refinery population was estimated from the data in Table 3-3. Non-generating refineries for a particular waste stream were defined as those refineries reporting a zero generation rate, the waste stream discharging the sewer system, and not reporting any generation rate for that waste stream. The estimates of the percentage of generating refineries were multiplied by the generation factors for the generating refineries to compute the generation factors for all refineries. The total estimation procedure is contained in Appendix III. Table 3-4 contains the generation factors for all refineries and the estimates of the percent of generating refineries and 95 percent confidence intervals for each. The confidence interval for the generation factor for Stream 19 is unreasonably large because of the extreme variability in the few generation rates reported: therefore, Stream 19 was dropped from further consideration. The confidence intervals are based on the variability in the data and do not allow for biases mentioned in Section 3.2. Therefore, the confidence intervals may be an under-estimate of the uncertainty in the generation factors.

3.4 Comparison with Previous Studies

Two previous studies have estimated solid waste generation for the petroleum refining industry. The first study (JA-216) was conducted by Jacobs Engineering Company in 1974 for EPA-Office of Solid Waste. Jacobs sampled waste streams at sixteen refineries and used the resulting data to calculate generation factors and national solid waste generation by waste stream. The second study (EN-818) was conducted by API in 1976. API sent data request forms to all the operating U.S. refineries. The responses received represented 57 percent of the refining capacity at that time. API used the data from the responses to estimate national solid waste generation by waste stream.

In comparing the results of these studies, it would be helpful to have a measure of the uncertainty in the estimated generation factors for each study. The confidence intervals in Table 3-4 serve that purpose for this study. However, no error bounds for the generation factors in either the Jacobs or API reports were given. Therefore, the confidence intervals in Table 3-4 will be used as a basis of comparison, even though they are actually too narrow for this purpose since they account for the uncertainty in the generation factors in this study only.

The comparison will be made by determining if the generation factors from the Jacobs and API reports fall within the error bounds of the generation factors developed in this study. If they do, then there is evidence that the differences in generation factors are due to the expected differences in refineries. If they do not fall within the error bounds, then possibly other factors or biases are causing the differences.

Jacobs reported solid waste generation factors based on medians; therefore, the generation factors in Table 3-4 are not comparable to these factors. In order to check the reasonableness of the factors from this study against Jacobs' factors, the medians from this study, not including the refineries not generating, were compared with the medians from the Jacobs report. The refineries not generating were excluded because Jacobs' medians included only generating refineries. Table 3-5 contains these medians and 95 percent confidence intervals for medians

TABLE 3-5

COMPARISON OF JACOBS AND EPA-OAQPS GENERATION FACTORS

Stream Number (See Table 3-2)	Median Solid Waste Generation Factors (Dry metric tons/yr. per 1000 barrels (Stream day)		95% Confidence Intervals for EPA-OAQPS Medians
	Jacobs	EPA-OAQPS	
1	1.38	0.58	0.19-3.13
2	2.00	1.90	0.09-4.52
3	0.33	0.02	0.006-0.51
4	2.2	0.96	0.45-2.6
5	46.0	0.01	0.01-0.22
6	0.17	0.13	0.04-1.2
7	-	0.19	0.004-0.51
8	0.75	0.06	0.01-0.28
9	3.64	1.42	0.7-11.6
10	0.93	0.22	0.06-0.57
11	215.6	0.21	0.02-1.04
12	21.7	0.64	0.03-5.44
13	0.8	2.20	0.17-9.5
14	12.6	0.50	0.04-1.85
15	5.45	4.04	3.18-5.95
16	0.28	1.60	0.02-6.34

from this study. Five of the fifteen medians from the Jacobs report, Streams 5, 10, 11, 12, and 14 do not fall with the confidence intervals. The median for Stream 10 is only slightly larger than the upper confidence bound; so, if the uncertainty associated with the median were accounted for, it would probably fall within the interval. The medians for the other four streams are quite large and are in definite disagreement with the results of this study. The medians for these streams are based on only two or three samples; therefore, the possibility exists that the medians are biased.

Table 3-6 contains the mean generation factors for the API study and this study and the confidence intervals for the factors from this study. The API generation factors were not presented explicitly in the API report; therefore, the factors had to be calculated by dividing the total solid waste generation for each waste stream by the capacity of the refining industry as cited in the report. The API generation factors for Streams 13 and 14 are the only factors that do not fall within the EPA-OAQPS confidence intervals. The factors for the streams are only slightly outside the confidence bounds. If the uncertainty associated with the factors was accounted for, they would probably fall within the intervals.

3.5 Extrapolation of Data

In order to obtain an estimate of the annual solid waste generation of the entire U.S. petroleum refining industry, the generation factors for all refineries in Table 3-4 were multiplied by the crude capacity of all operating refineries as given in the Annual Refining Survey published in the Oil and Gas Journal (CA-673). The resulting estimates of total generation by waste stream were then summed to obtain a total for all waste streams. The confidence intervals for the generation factors were also multiplied by refinery capacity to obtain confidence intervals for the

TABLE 3-6

COMPARISON OF API AND EPA-OAQPS GENERATION FACTORS

Stream Number (See Table 3-2)	Mean Solid Waste Generation Factors (Dry metric tons/year per 1000 barrels/stream day)		95% Confidence Intervals for EPA-OAQPS Means
	API	EPA-OAQPS	
1	-	3.37	0.55 - 16.3
2	1.46	7.94	0.93 - 52.4
3	-	0.039	0.005 - 0.21
4	4.56	2.90	1.22 - 5.34
5	-	0.051	0.0045 - 4.1
6	-	0.82	0.14 - 3.2
7	-	1.22	0.013 - 8.5
8	-	0.25	0.061 - 0.79
9	2.25	4.32	1.4 - 9.9
10	-	0.14	0.031 - 0.46
11	-	2.55	0.24 - 21.5
12	0.39	1.94	0.12 - 23.9
13	1.12	5.55	1,27 - 20.5
14	2.76	0.14	0 - 2.7
15	3.60	5.64	2.1 - 7.0
16	-	2.03	0.05 - 46.3
17	-	0.001	0 - 0.02
18	-	-	-
19	-	-	-
20	-	0.13	0.008 - 1.32

TABLE 3-7

ANNUAL SOLID WASTE GENERATION OF THE ENTIRE U.S. PETROLEUM REFINING INDUSTRY

Waste Stream (See Table 3-2)	Total Generation (metric tons/year)	95% Confidence Interval for Total Generation (metric tons/year)
1	59,380	9,690 - 28,720
2	139,900	16,390 - 923,200
3	690	90 - 3,700
4	51,090	21,500 - 94,090
5	900	80 - 72,200
6	14,450	2,470 - 56,460
7	21,500	230 - 149,800
8	4,400	1,070 - 13,920
9	76,110	24,670 - 174,400
10	2,470	550 - 8,100
11	44,930	4,230 - 378,800
12	34,180	2,100 - 421,100
13	97,790	22,380 - 361,200
14	2,470	0 - 47,570
15	99,370	37,000 - 123,300
16	35,770	880 - 815,800
17	18	0 - 350
18	--	-
19	--	-
20	2,290	140 - 23,300
Total	687,708	143,470 - 3,695,950

estimates of total generation by waste stream. The lower bounds and the upper bounds of the confidence intervals were then summed to obtain a confidence interval for the total generation for all waste streams. These figures are presented in Table 3-7.

The estimate of total annual solid waste generation for the refining industry developed by this study is approximately twice the total reported by API and three times the total reported by Jacobs. However, the API total of 357,000 metric tons/year and the Jacobs total of 240,000 metric tons/year both fall within the confidence interval for the total from this study. Since the API and Jacobs totals fall within the confidence limits, there is evidence that the differences in the totals are due to the expected differences in refineries.

4.0 HYDROCARBON EMISSIONS

One objective of the EPA-OAQPS study was to estimate the national VOC atmospheric emissions resulting from refinery solid waste treatment and disposal. Petroleum refineries are a known source of VOC emissions. Large quantities of organics flow through refineries, so that process units, storage units, waste treatment systems, and fugitive sources (leaks) may possibly emit volatile organics. Volatile hydrocarbons may also become part of a solid waste stream, along with hydrocarbons of lower volatility. Exposure of the solid waste to the atmosphere, which occurs during common handling, transport, and disposal methods, may allow some or all of the volatiles to evaporate.

4.1 Data Analysis

4.1.1 Phase Composition of Waste Streams

The generation rate and gross phase composition (solid, aqueous, hydrocarbon) for twenty major refinery solid waste streams were obtained in the EPA-OAQPS survey. The phase composition data is summarized in Table 4-1, along with values from the API study for comparison. Overall, the two studies are in close agreement.

4.1.2 Hydrocarbon Content of Refinery Solid Waste

The generation rate data and the phase composition data may be combined to determine the hydrocarbon content of all United States refinery solid wastes. Hydrocarbon content, on a dry weight basis, was calculated for each stream, and multiplied by the appropriate generation rate to obtain the hydrocarbon generation rate for each stream; the result is presented in Table 4-2. As shown in the table, hydrocarbons in DAF Skimmings, Slop

TABLE 4-1

EPA - OAQPS SURVEY

SUMMARY OF REPORTED PHASE DATA

WATER, SOLID, AND HYDROCARBON CONTENT OF REFINERY SOLID WASTE STREAMS

(Compositions in Weight Percent)

Sample Phase	Slop Oil Emulsion Solids	Storm Runoff Silt	Exchanger Bundle Cleaning Sludge	API Separator Sludge	Non-Leaded Product Tank Bottoms	Crude Tank Bottoms	Other Storage Tank Bottoms	Leaded Tank Bottoms	DAF Float
Water									
Range	0-94	15-94	0-96	0-98	0-99	0-99	0-99	0-99	3-99
Mean	34	44	50	59	27	39	38	35	74
No. of Responses	17	12	8	26	11	14	17	10	17
Solids									
Range	3-90	6-100	3-100	0-60	1-100	6-100	0-99	0-100	0.5-93
Mean	27	52(61)	28	18(22)	40(24)	23(11)	32	46(29)	10(6)
No. of Responses	13	14	9	25	11	12	17	10	17
Hydrocarbons									
Range	1-80	0-35	4-17	0.2-90	0-86	0-88	0-86	0-27	0.2-90
Mean	35	5(4)	4	19(13)	23(33)	34(53)	21	7(33)	17(11)
No. of Responses	14	13	8	28	13	18	11	13	18

Sample Phase	Kerosene Filter Clays	Other Filter Clays	Neutralized HF Alky. Sludge	Waste Bio-Sludge	Once-Through Cooling Sludge	FCC Catalyst Fines	Coke Fines	Spent Amines
Water								
Range	0-50	0-98	39-98	0-99	75-80	0-40	<1-70	6-99
Mean	16	24	53	81	77	3	16	65
No. of Responses	3	10	5	20	2	12	7	10
Solids								
Range	50-95	1-100	2-100	1-79	20-25	60-80	5-99	1-92
Mean	77(70)	57(73)	45	11(9)	22(47)	88(92)	73	23
No. of Responses	3	10	5	19	2	19	8	10
Hydrocarbons								
Range	0-13	0-48	<1-75	0-28	0-0	<0.01-<1	<1-70	<0.1-100
Mean	5(11)	14(19)	3	4(6)	0(2)	<1	13	11
No. of Responses	5	11	8	17	2	14	8	10

Note: API Refinery study data for similar waste streams are shown in parentheses.

TABLE 4-2

EPA - OAQPS SURVEY
TOTAL HYDROCARBONS* IN REFINERY SOLID WASTES
(Total U. S. Refineries)

Solid Waste Stream	Hydrocarbons in Waste Streams (Metric Tons/Year)	Percent of Total
Dissolved Air Flotation	49,470	29.2
Slop Oil Emulsion Solids	31,470	18.6
API Separator Sludge	23,500	13.9
Biosludge	20,540	12.1
Storm Runoff Silt	12,590	7.4
Other Filter Clays	8,090	4.8
Crude Tank Bottoms	8,090	4.8
Other Tank Bottoms	7,310	4.3
HF Alklation Sludge	2,050	1.2
Coke Fines	5,370	3.2
Leaded Tank Bottoms	480	0.3
Non-Leaded Tank Bottoms	290	0.2
Kerosene Filter Clays	150	0.1
Exchanger Bundle Cleaning Sludge	60	0.04
Spent Amines	5	0
FCC Catalyst Fines	0**	0
Once-through Cooling Water Sludge	0	0
TOTALS:	169,465	100.14

Notes:

* Hydrocarbons were defined as the portion of the waste stream present in the liquid organic phase (distinct from the aqueous and solid phases).

** Reported Composition <1% hydrocarbon.

Oil Emulsion Solids, API Separator Sludge, and Biosludge comprise about 75 percent of total refinery solid waste hydrocarbons.

The total hydrocarbon content of refinery solid waste was found to be approximately 190,000 tons/yr. Although the potential exists for hydrocarbon recovery from solid wastes, recovery practices vary greatly among the refineries and many wastes are not treated before disposal. Of the four streams which are major hydrocarbon sources, only DAF Skimmings are widely treated for hydrocarbon recovery (EN-821). Therefore, a major part of the hydrocarbon phase of the wastes is disposed.

4.1.3 Estimation of VOC Emissions

Only a fraction of the total hydrocarbon content will be released to the atmosphere; the amount is primarily dependent on volatility. One way to express the sensitivity of total hydrocarbon emission to volatility is shown in Figure 4-1. If the volatile organic fraction of solid waste hydrocarbons was known, then an upper bound for VOC emissions could be determined by the figure. For instance, assuming that 10 percent of the total hydrocarbons are volatile, refinery solid waste VOC emissions could approach 19,000 tons/yr. It may be expected that only a few percent of the hydrocarbons are volatile, due to upstream processing in the refinery. Actual emissions would be less than the upper bound, depending on waste source, treatment and disposal, and mass transport effects. Volatility, however, is the most important indication of VOC emission potential.

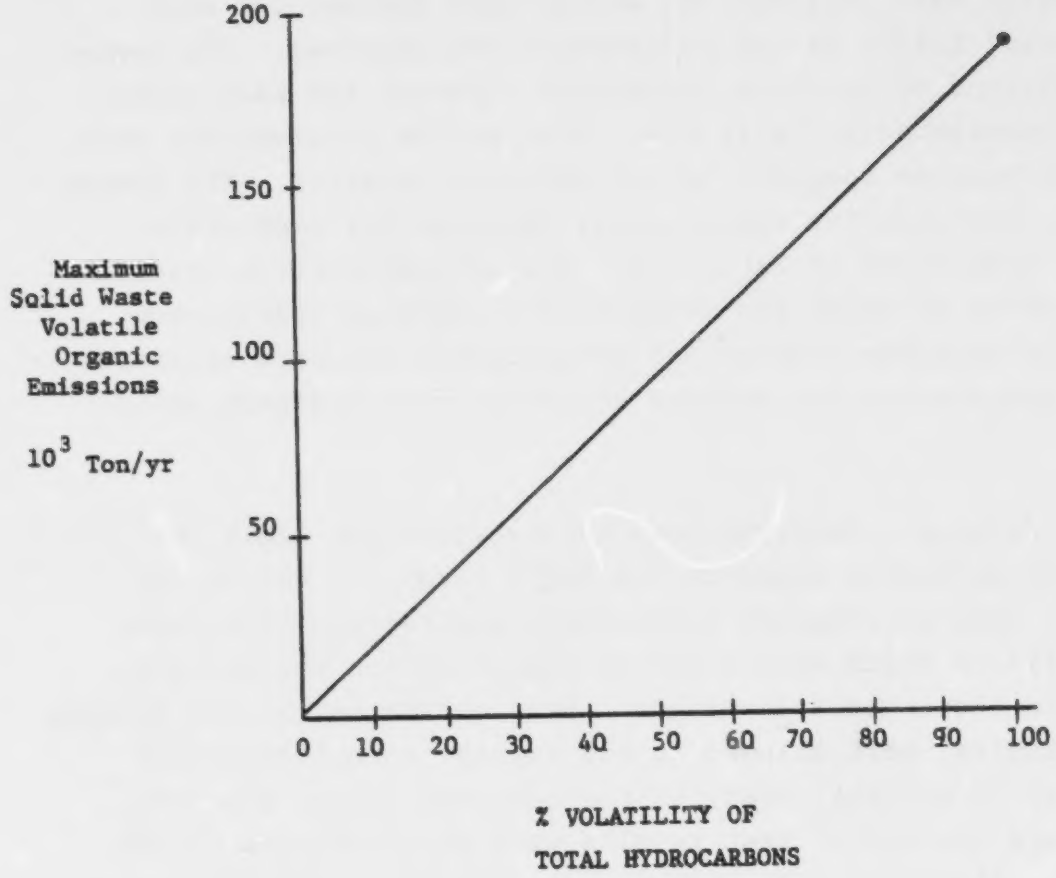


FIGURE 4-1

ORGANIC EMISSION VERSUS

VOLATILITY OF HYDROCARBON PHASE

4.2 Data Limitations

The EPA-OAQPS survey did not produce a sufficient data base to accurately estimate volatile organic emissions. Although the requested data included VOC and benzene content for each waste stream, little usable information was received. The number of observations of volatile components reported for each waste stream is presented in Table 4-3. Some of the observations were not usable because specific values were not reported. The number of usable, quantitative observations reported for each waste stream is also shown in Table 4-3. The 35 quantitative observations reported to OAQPS are inadequate to develop hydrocarbon and benzene emission factors and subsequently accurate estimates of total hydrocarbon and benzene emissions from refinery solid waste.

Missing information and estimated values limit the accuracy of estimates based on the OAQPS data. In the survey responses, lack of standard definitions and testing procedures for volatile organics were cited as justification for not submitting the requested information. Best estimates, in the absence of test results, were allowed in the survey, with a requested accuracy of 20 percent. Many of the reported values are estimates, since analytical test results were not available to the companies. Also, the wide variation in reported compositions may indicate that some waste samples were fresh from refinery sources, while other samples had been air dried for several days or had undergone other treatment.

4.3 Factors Controlling Volatile Emissions

An accurate estimate of VOC emissions from solid wastes cannot be simply based on hydrocarbon volatility, since the emission of volatiles is a complex mass transport process. Solid

TABLE 4-3

VOLATILE COMPONENTS OF WASTE STREAMS REPORTED IN EPA-OAQPS SURVEY

		Volatile Organic Carbon		Total Light Hydrocarbons		Benzene	
No.	Waste Streams	Number of Data Points	Number of Useable(1) Data Points	Number of Data Points	Number of Useable(1) Data Points	Number of Data Points	Number of Useable(1) Data Points
1	Slop Oil Emulsion Solids	1	0	0	0	6	0
2	Silt from Stormwater Runoff	1	1	0	0	6	1
3	Exchanger Bundle Cleaning Sludge	0	0	0	0	4	0
4	API Separator Sludge	1	0	0	0	11	3
5	Non-Leaded Gasoline Tank Bottoms	0	0	0	0	4	4
6	Crude Tank Bottoms	0	0	1	0	6	2
7	Other Storage Tank Bottoms	0	0	1	0	7	1
8	Leaded Gasoline Tank Bottoms	0	0	2	0	7	4
9	Dissolved Air Flotation Skimmings	1	0	0	0	10	6
10	Kerosene Filter Clays	0	0	0	0	1	0
11	Other Filter Clays	1	0	0	0	1	0
12	HF Alkylation Sludge	2	2	0	0	4	2
13	Waste Bio-Sludge	1	1	0	0	6	3
14	Once-Through Cooling Water Sludge	0	0	0	0	0	0
15	FCC Catalyst	1	1	0	0	5	1
16	Coke Fines	0	0	0	0	6	0
17	Spent Amines	0	0	0	0	4	0
18	Salts from Regeneration	0	0	0	0	0	0
19	Ship and Barge Ballast	0	0	0	0	2	0
20	Other	1	1	0	0	5	2

---

(1) Useable data points were defined as analyses reported as a specific value for the constituent.

waste composition is only one of several physical and chemical factors which affect VOC emissions; some of these are listed in Table 4-4.

Factors which determine the exposure of solid wastes to the air may have an important effect on VOC emission. Long exposure time and large exposed surface area would give the most opportunity for volatile evaporation. However, evaporation may be so rapid that all VOC emissions take place in preliminary dewatering or transportation, so that an actual disposal method is not significant. Also, evaporation of volatiles in process sewer lines may cause VOC emissions at that point. Since waste handling procedures vary widely among refineries, it is difficult to estimate at which point the volatiles may be emitted from solid wastes. But, if volatiles are present in the fresh waste stream, there is ample opportunity for air emissions during treatment and disposal.

Mass transport of VOC from the solid waste depends on both chemical composition and physical properties. The concentration of volatiles in the hydrocarbon phase is the driving force behind VOC mass transport. The vapor pressure and molecular weight of each chemical species affect the evaporation rate, as do oil-water phenomena and interphase binding. The VOC emission rate may be low even with a rapid evaporation rate, since transport of volatiles in the sludge may be the controlling factor. For instance, rapid evaporation may form a crust or impervious layer at the surface which prevents further VOC emission from the bulk of the waste. No information on the occurrence of these phenomena in refinery solid waste is believed to exist.

TABLE 4-4

FACTORS AFFECTING VOE FROM SOLID WASTES

1) Disposal Site Construction
   - covered or open
   - sand bed drainage
   - land farm or landfill
   - dilution in lagoon
2) Composition
   - phase composition (overall)
   - hydrocarbon phase composition (volatiles)
   - concentrations in each phase
3) Physical Transport in Sludge
   - crusting - impervious layer
   - cracking
   - volatile diffusion
4) Exposure Time
   - drying - open air
   - tilling and soil aeration - land farm
5) Transportation and Pre-Treatment Handling
   - wastewater process units
   - open dump truck or tank car transport
   - spreading method
6) Weather
   - temperature
   - wind
   - sun
   - rain
   - humidity
7) Waste Deployment
   - thick or thin layer
   - packed or unpacked
   - density
8) Mixing of Waste Streams
9) Oil-Water Phenomena
   - surface oil layer
   - emulsification
10) Inter-Phase Binding
   - hydrocarbon-water solubility
   - hydrocarbon-solid adsorption

4.4 Supplementary Data Collection Program

The most important data missing from the OAQPS survey results are the amounts of volatile hydrocarbons present in each stream. Standard test procedures specifically designed for VOC in solid wastes can be developed and applied to obtain the missing information. This would permit estimation of the maximum potential VOC emissions. To estimate actual VOC emissions, in-lab simulation of waste disposal methods are necessary to measure multiphase mass transport of volatile organics.

A supplemnetary sampling program will provide the data required for an accurate estimate of VOC emissions from refinery solid wastes. The more complete characterization of solid waste streams obtained in such a program would have many valuable uses. These would include:

- Better estimation of solid waste compositions and generation rates through statistically designed survey methods
- Provision of required data for VOC emissions estimate
- Identification of toxic and hazardous compounds
- Better data base for design of solid waste treatment and disposal methods
- Identification of valuable constituents for possible resource recovery

A suggested sampling program is presented in Appendices IV and V which addresses the following factors:

- Refinery complexity, crude slate and location
- Solid waste stream characteristics
- Number of samples required
- Analytical parameters
- Development of reproducible sampling/sample preservation techniques.

Appendix IV discusses alternative schemes for selecting a representative sample of the entire U.S. refining industry. A modification to the refinery sampling program developed by Arthur D. Little, Inc. (ADL) is presented. The suggested program utilizes the Bureau of Mines Petroleum Administration for Defense (PAD) refinery classes to serve as the basis for a stratified sampling approach to collect the required refinery waste samples. The stratified sample design eliminates bias from the sample data and therefore permits more accurate estimate of waste volumes and characteristics.

Appendix V describes the design of a supplementary sampling program that could be pursued. Table 4 in this Appendix shows the cost and the precision of the estimate of constituent content for various sampling programs. From the table, given a desired level of precision for the estimate, a sampling program and its associated cost can be found.

4.5 VOC Emissions from Other Industries

The petroleum refining industry is only one of many potential sources of solid wastes containing organic solvents. In order to make a realistic estimate of national atmospheric emission rates of VOCs from organic solid wastes, other industries must be considered.

Solid wastes containing volatile organic compounds are generated by industry as the result of both primary production activities and hydrocarbon recovery and reprocessing. Many industrial production processes have been studied from the standpoint of organic emissions from vapor-emitting point and fugitive sources. However, liquid and solid solvent-contaminated waste streams and the resultant organic emissions have not been studied adequately. Reprocessing and recovery industries closely related to the refining industry, such as the petroleum re-refining and solvent reclamation facilities have process streams with characteristics common to refineries. Solid waste streams from these industries may also contain VOCs similar to refining wastes. However, it is beyond the scope of this report to analyze in detail the waste streams generated by other industries.

5.0 SOLID WASTE MANAGEMENT PRACTICES

Numerous solid waste streams (which in this report include sludges) are generated by refinery processes. The quantities and compositions of these streams have been identified previously in this report. This section will focus on:

- Source control
- Treatment
- Final disposal

5.1 Source Control

Source control can be defined as the reduction or containment of plant emissions at their point of generation. Instead of continually investing in more extensive pollution control equipment to meet new regulations, refiners are making significant moves to reduce wastes generated. By continuously implementing new source control methods, refiners anticipate the constantly changing regulations and minimize the effort and costs of compliance. One approach to source control is the addition or alteration of equipment. For instance, installation of tank mixers in crude and other storage tanks minimizes the deposition of bottoms sludge.

Another approach is through operational or procedural changes. Two examples are:

- Shutdown planning. The amounts and qualities of oily wastes are predetermined and handled appropriately in the event of an equipment shutdown.
- Internal refinery permit system. An oily stream can be released to the oily drains only with the approval of the Environmental Department.

Although source control has greater potential application to refinery wastewaters, some utility in reducing solid waste emissions is also possible. One major area currently undergoing extensive study is the reduction of waste biosludge by lessening the load on the wastewater treatment system. For example, water reuse is a common strategy for reducing wastewaters.

With the increased promulgation of environmental regulations and rising costs of pollution control, in many cases the most cost-effective approach to management of refinery sludges will be to locate and reduce emissions at the source.

5.2 Treatment

Up until the last few years, most refiners considered solid waste disposal as a low priority item and a profit drain. Consequently, convenience rather than environmental concern dictated use of sludge pits and lagoons, usually located at the back of refinery property. Little attention was given to leachate, air emissions, or ultimate disposition of pollutants contained in these pits. If solid wastes were consigned to a contractor, the material was considered properly disposed of as soon as it left the refinery.

The abundance of environmental regulations has forced refiners to critically evaluate their pollution abatement systems. One important aspect of these systems is the management of solid waste. The process descriptions which follow evaluate the existing and planned solid waste management techniques on a cost/performance basis. Many costs are updated to December 1978; cost data given in graphical form are not updated but rather the cost index values are supplied to permit the reader to bring the data up to date.

The process descriptions in Appendix I may be divided into three sections:

(1) Proven treatment technologies currently in use in refineries:

- Vacuum filtration
- Pressure filtration
- Centrifugation
- Dewatering lagoons
- Aerobic digestion
- Anaerobic digestion
- Chemical fixation

(2) Proven treatment technologies potentially usable in refineries:

- Sand drying beds
- Wet-air oxidation
- Composting

(3) Unproven treatment technologies with respect to refinery sludges that may have potential utility:

- BEST/solvent extraction process

Thermal drying as a treatment technology is not applicable to the refining industry. A high potential exists for odor problems and evaporation of hydrocarbons. Drying is most amenable to recovery of a valuable chemical of solid substance for resale. Few refinery sludges, if any, meet these criteria.

5.3 Final Disposal

Much indecision on final disposal techniques currently exists in the refinery industry. Most of this is due to pending regulations, primarily the Resource Conservation Recovery Act (RCRA) regulations for environmentally acceptable disposal means, and the potential classification of many refinery wastes as hazardous. The current technologies that this subsection of the report includes are:

- Incineration
- Landfarming
- Landfilling
- Ponding
- Disposal wells
- Ocean disposal

Only landfarming can truly be considered an ultimate disposal technique because the wastes are degraded into matter that becomes a part of the soil. Although anaerobic degradation theoretically occurs in landfills, some of those that have been recently reopened showed no significant deterioration of the oily wastes. Ponding, disposal wells and ocean disposal are merely storage techniques with no significant waste degradation. Incineration generates air pollutants and ash residues that need disposal.

Ocean disposal, deep well injection, and ponding are being phased out due to their adverse environmental impact. The use of landfarming, however, is increasing significantly where land is available. The possibility of farming organic wastes from retired refinery sludge pits after recovering and recycling oil is being seriously considered.

Contracting wastes to local municipalities or private disposal firms is prevalent in the petroleum refining industry. Various proposed regulations will affect this practice which may increase on-site disposal activities. To write effective standards for air emissions from solid waste disposal practices, the refiners' intentions with respect to on-site versus contracted disposal must be estimated.

5.4 Process Descriptions

In Appendix I, both existing and planned techniques in treatment and final disposal are identified, described, and evaluated according to their development status, performance, and cost and energy requirements. Particular attention is devoted to any secondary pollutants generated by processing of solid wastes, e.g., air emissions from incineration of oily wastes. Figure 5-1 depicts a matrix summary of the application of proven and unproven technologies to the various waste streams.

Waste Stream	Sludge Treatment											Ultimate Disposal					
	Vacuum Filtration, P.	Pressure Filtration, P.	Centrifugation, P.	Dewatering Lagoons, P.	Aerobic Digestion, P.	Anaerobic Digestion, P.	Chemical Fixation, P.	Sand Drying Beds, P.	Wet-Air Oxidation, P.	Composting, P.	BEST/Solvent Extraction, P.	Landfilling, P.	Landfarming, P.	Incineration, P.	Disposal Lagoons, P.	Disposal Wells, P.	Ocean Disposal, P.
API Separator Sludge	2	1	2	1	4	4	1	4	2	2	3	1	1	1	1	4	4
Nonleaded Gasoline Tank Bottom	4	4	4	1	4	4	1	2	4	2	3	1	1	4	2	4	4
Crude Tank Bottoms	4	4	4	1	4	4	1	2	4	2	3	1	1	4	1	4	4
Other Storage Tank Bottoms	4	4	4	1	4	4	1	2	4	2	3	1	1	4	1	4	4
DAF Skimmings	2	1	2	1	4	4	2	4	2	2	3	1	1	1	1	2	4
Waste Biosludge	1	1	1	2	1	1	1	2	2	2	3	1	1	1	1	2	2
Slop Oil Emulsion Solids	2	1	2	1	4	4	2	4	2	2	3	1	1	1	1	4	4
Silt from Storm Water Runoff	4	4	4	1	4	4	1	2	4	4	4	1	1	4	1	4	4
Once-Through Cooling Water Sludge	2	2	2	1	4	4	2	2	4	4	4	1	1	4	1	4	4
Kerosene Filter Clays	4	4	4	4	4	4	1	4	4	4	4	1	1	4	4	4	2
Other Filter Clays	4	4	4	4	4	4	1	4	4	4	4	1	1	4	4	4	2
Exchanger Bundle Cleaning Sludge	4	4	4	1	4	4	2	2	4	4	4	1	1	4	2	4	4
Neutralized HF Alkylation Sludge	4	4	4	1	4	4	2	2	4	4	4	1	1	4	1	4	4
FCC Catalyst Fines	4	4	4	4	4	4	1	4	4	4	4	1	1	2	1	4	2
Spent Amines	4	4	4	1	2	2	2	2	4	2	4	1	1	1	1	4	4
Leaded Gasoline Tank Bottoms	4	4	4	2	4	4	1	2	4	2	3	1	1	4	1	4	4
Coke Fines	4	4	4	4	4	4	2	4	4	4	4	1	1	4	1	4	2

Key:
1 Proven technology that is currently being applied to this waste stream.
2 Proven technology that is currently being applied to industrial and/or municipal waste streams, but is not currently being applied to this waste stream.
3 Unproven technology that might be applicable to this waste stream.
4 Proven or unproven technology that is not applicable to this waste stream.

Note: Each waste stream has been considered individually, not in combination with others. This limits the applicable technology, but the streams must still be considered individually because it is impossible to consider all the possible combinations.

The results listed above in Figure 5-1 include both current and/or past application to the particular waste stream.

The consideration of the application of these technologies includes wastes processed on-site and those consigned to a contractor.

The results listed in the matrix were not based upon the frequency of application of a technology to the given waste streams.

FIGURE 5-1

MATRIX SUMMARY OF CONTROL TECHNOLOGIES
AND REFINERY WASTE STREAMS

BIBLIOGRAPHY

AI-038 Aitchison, J., "On the Distribution of a Positive Random Variable Having a Discrete Probability Mass at the Origin," American Statistical Association Journal, 50, (9), 1955, 901-908.

AM-065 American Petroleum Inst., Div. Statistics & Economics, Annual Statistical Review, U.S. Petroleum Industry Statistics 1956-1972. Washington, D.C., 1973.

AM-046 Ambler, Charles M., "Centrifuge Selection," Chem. Eng. 78(4), 55 (1971).

AM-062 American Petroleum Inst., Div. of Refining, Manual on Disposal of Refinery Wastes. Volume on Liquid Wastes, First edition. Washington, D.C., 1969.

AS-070 Ashbrook, Simon and Hartley, "Sludge Dewatering with Klampress," brochure. Houston, TX, undated.

BE-499 Benjes, Henry H., Jr., Cost Estimating Manual--Combined Sewer Overflow Storage and Treatment, final report. EPA Contract No. 68-02-2186, EPA 600/2-76-286. Cincinnati, OH, EPA, Municipal Environmental Research Laboratory, Systems & Engineering Evaluation Branch, Wastewater Research Division, Dec. 1976.

BI-043 Bitler, John A. and L. John Minnick, "Lime-Sulfur Dioxide Scrubbing System and Technology for Utilization of Underflow Sludge," Presented at the Nat'l. Lime Assoc. Annual Convention, 70th, Hot Spring, VA, 1972.

BO-196 Bombaugh, K. J., et. al., Sampling and Analytical Strategies for Compounds in Petroleum Refinery Streams, EPA Contract No. 68-02-1882. Radian Corp., Austin, TX, Sept. 15, 1975.

BO-328 Bollinger, John C. and Jeffrey L. Shumaker, Control of Volatile Organic Emissions from Solvent Metal Cleaning, EPA 450/2-77-022, OAQPS 1.2-079, Research Triangle Park, NC, Environmental Protection Agency, Office of Air Quality Planning and Standards, Office of Air and Waste Management, November 1977.

CA-099 Cantrell, Ailleen, "Annual Refining Survey," Oil and Gas Journal, April 2, 1973.

BIBLIOGRAPHY (Continued)

CA-236 Cantrell, Ailleen, "Annual Refining Survey," Oil and Gas Journal, April 7, 1975.

CA-279 Cantrell, Ailleen, "Annual Refining Survey," Oil and Gas Journal, April 1, 1974.

CA-339 Cantrell, Ailleen, "Annual Refining Survey," Oil and Gas Journal, March 29, 1976.

CA-673 Cantrell, Ailleen, "Annual Refining Survey," Oil and Gas Journal, March 20, 1978.

CH-196 Cheremisinoff, Paul N. and Richard A. Young, eds., Pollution Engineering Practice Handbook. Ann Arbor, MI, Ann Arbor Science, 1975.

CH-353 Cheremisinoff, Paul N., "Biological Wastewater Treatment," Pollution Engineering 8(9), 32-8, 1976.

CH-447 Cheremisinoff, P. N., "Sludge Handling and Disposal," Poll. Eng. 8(1) 22, 1976.

CL-039 Clark, John W., Warren Viessman, Jr., and Mark J. Hammer, Water Supply and Pollution Control, 2nd ed. Scranton, PA., International Textbook Co., 1971.

CO-698 Colley, J. D., et. al., Assessment of Technology for Control of Toxic Effluents from the Electric Utility Industry, Revised, DCN 78-200-187-09-08, EPA Contract No. 68-02-2608, Work Assignment 9. Austin, TX, Radian Corp., Dec. 1977.

CR-154 Cross, Frank L., Jr., "Control and Treatment of Wastewater," Poll. Eng. 9(1), 99-105, 1977.

CU-082 Culp/Wesner/Culp, Estimated Costs of the B.E.S.T. System and Other Methods for Treatment and Use or Disposal of Municipal Wastewater Sludges. Jan. 1977.

CU-087 Culp, R. L., Handbook of Advanced Wastewater Treatment, 2nd Edition, New York, Van Nostrand Reinhold, 1978.

DR-048 Drew, J. W., "Design for Solvent Recovery," Chem. Eng. Prog. 71(2), 92-99, February, 1975.

BIBLIOGRAPHY (Continued)

EC-008 Eckenfelder, W. Wesley, Jr., Industrial Water Pollution Control. N.Y., McGraw-Hill, 1976.

EN-295 Environmental Protection Agency, Process Design Manual for Upgrading Existing Wastewater Treatment Plants. Oct. 1974.

EN-325 Environmental Protection Agency, Technology Transfer, Process Design Manual for Sludge Treatment and Disposal. EPA 625/1-74-006, October 1974.

EN-407 Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category, EPA Contract No. 68-01-0598, Washington, D.C., April, 1974.

EN-602 Environmental Protection Agency, Office of Solid Waste Management Programs, Decision-Makers Guide in Solid Waste Management. SW-500. 1976.

EN-605 Environmental Protection Agency, Office of Solid Waste Management Programs, Disposal of Hazardous Wastes, Report to Congress. SW-115. 1974.

EN-818 Engineering Science, Inc., The 1976 API Refinery Solid Waste Survey, Pt. 1, Solid Waste Quantities, Draft Final Report. Austin, TX, Jan. 1978.

EN-819 Environmental Protection Agency, Effluent Limitations Guidelines (BATEA) New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category, Washington, D.C., March, 1978.

EN-820 Environmental Protection Agency, (OAQPS), Refinery Waste Disposal - Responses to April 11, 1978, Section 114

EN-820 Environmental Protection Agency, (OAQPS), Refinery Waste Disposal - Responses to April 11, 1978, Section 114 Information Request, 1978.

EN-821 Engineering-Science, Inc., The 1976 API Refinery Solid Waste Survey, Pt. 2, Solids Management Practices, April 1978, Austin, TX.

BIBLIOGRAPHY (Continued)

FA-178 Environmental Protection Agency (OSW), Information About Hazardous Waste Management Facilities, Publication SW-145, Prepared by D. Farb and S. D. Ward, February 1975, Cincinnati, OH.

FE-055 Ferrel, James F., "Sludge Incineration," Poll. Eng. 1973 (March) 36.

FI-163 Finney, D. J., "On the Distribution of a Variate Whose Logarithm is Normally Distributed," Journal of the Royal Statistical Society, Series B, 7 (1941), 155-161.

GO-279 Goldstein, D. J. and David Yung, Water Conservation and Pollution Control in Coal Conversion Processes, Final Report, EPA Contract No. 68-02-2207, EPA 660/7-77-065. Cambridge, MA., Water Purification Associates, June 1977.

HU-236 Hulswitt, Charles, (Astro Mettalurgical Corp., Wooster, OH), Private Communication will Bill Arnold, 7 Feb. 1978.

JA-216 Jacobs Engineering Co.,"Alternatives for Hazardous Waste Management in the Petroleum Refining Industry," Draft Final Report, EPA Contract No. 68-01-4156. Pasadena, CA, April 1977.

JO-273 Jones, Jerry L., et. al., "Municipal Sludge Disposal Economics," Env. Sci. Tech. 11(10), 968 (1977)

KN-053 Knowlton, H. G., "Source Control in Petroleum Refineries," Presented to NPRA Annual Meeting, San Antonia, TX, March, 1978.

KN-054 Knowlton, H. E. and J. E. Rucker, "An Overview of Petroleum Industry Use of Landfarming," Presented at the 71st Annual AIChE Meeting, Miama Beach, FL, Nov. 1978.

KN-055 Knowlton, H. E. and J. E. Rucker, "Refinery Oily Waste Treatment and Disposal Techniques and Their Potential Application to Oil Spill Debris," Presented at the ASTM Symposium on Oil Spill Material Disposal, Denver, CO, Nov. 1978.

LE-380 Levin, J. E. and F. Scofield, "An Assessment of the Solvent Reclaiming Industry," Published in Preprints

BIBLIOGRAPHY (Continued)

170th ACS Meeting, Division of Organic Coatings & Plastics, 35(2), 416-418, Wapora, Inc., Washington, D.C., 1975.

LE-381 Lewis, Robert S., "Sludge Farming of Refinery Waste as Practiced at Exxon's Bayway Refinery and Chemical Plant," Presented at the Nat'l Conference on Disposal of Residues on Land, St. Louis, Sept. 1976.

LI-120 Liptak, Bela G., Environmental Engineers' Handbook, vols. 2 and 3. Radnor, PA., Chilton, 1974.

LI-150 (Arthur, D.) Little, Inc., The Impact of Producing Low Sulfur, Unleaded Motor Gasoline on the Petroleum Refining Industry, Draft Report, Vol. 1, Study Results and Planning Assumptions. EPA Contract No. 68-02-1332, Task Order No. 5, Cambridge, MA, Dec. 1975.

LI-151 (Arthur D.) Little, Inc., The Impact of Lead Additive Regulations on the Petroleum Refining Industry, Draft Report, Vol. 1, Study Results and Planning Assumptions. EPA Contract No. 68-02-1332, Task Order No. 7, Cambridge, MA, Dec. 1975.

LI-152 (Arthur D.) Little, Inc., Draft Copy: The Impact of SO_x Emissions Control on the Petroleum Refining Industry. EPA Contract No. 68-02-1332, Task Order No. 1, December, 1975.

MA-232 Marks, R. H., "Wastewater Treatment," Special Report, Power, June 1967.

MC-389 McCabe, Warren L. and Julian C. Smith, Unit Operations of Chemical Engineering, Third Edition. New York, McGraw-Hill, 1976.

ME-095 Metcalf and Eddy, Inc., Wastewater Engineering--Collection, Treatment, Disposal. McGraw-Hill Series in Water Resources and Environmental Egineering. New York, McGraw-Hill, 1972.

ME-218 Meserole, N. P., et. al., Review and Assessment of the Existing Data Base Regarding Flue Gas Cleaning Wastes, Draft Report. DCN 77-200-169-06, EPRI Research Projec 786-2, Task 1. Austin, TX, Radian Corp., Sept. 1977.

BIBLIOGRAPHY (Continued)

ME-292 Meyer, William R., "Solvent Broke," Cincinnati, OH, Vulcan, Cincinnati, Inc., undated.

ME-294 Metcalf and Eddy, Inc., *Wastewater Engineering: Treatment Disposal, Reuse*, 2nd Edition, New York, McGraw Hill, 1979.

PA-193 Patterson, W. L. and R. F. Banker, *Estimating Costs and Manpower Requirements for Conventional Wastewater Treatment Facilities*. Kansas City, MO., Black & Veatch, Oct. 1971.

PA-402 Patterson, R. L., "Difficulties Involved in the Estimation of a Population Mean Using Transformed Sample Data:, *Technometrics* 8, No. 3, (1966), 535-537.

PE-030 Perry, John H., *Chemical Engineers' Handbook*, 4th Ed. New York, McGraw-Hill, 1963.

PE-065 Peters, Max S. and Klaus D. Timmerhaus, *Plant Design and Economics for Chemical Engineers*, 2nd Edition. McGraw-Hill Chemical Engineering Series, New York, McGraw-Hill, 1968.

PE-224 Peeler, J. P. K. and K. L. Piggott, "Combined Gas Turbine-Steam Cycle for Power Generation, Part 2, Theoretical Study of a Coal-Fired System," *Inst. Eng. Aust. Mech. Chem. Eng., Trans. MC8*(2), 130-35 (1972).

PE-277 Perry, John H., *Chemical Engineers Handbook*, 5th Edition, New York, McGraw-Hill, 1973.

PO-079 Porter, H. F., J. E. Flood, & F. W. Rennie, "Filter Selection," *Chem. Eng. 78*(4), 39, 1971.

RA-596 Radian Corporation, *Final Report: Control Techniques for Volatile Organic Emissions from Stationary Sources*, EPA Contract No. 200-187-2308, Austin, TX, 1978.

RA-729 Radian Corporation, *Environmental Control Selection Methodology for a Coal Conversion Demonstration Facility*, Final Report. DCN 78-200-151-06-06, DOE Contract No. EX-76-C-01-2314, Austin, TX, Oct. 1978.

RO-423 Rosenberg, D. S., et. al., *Assessment of Hazardous Waste Practices in the Petroleum Refining Industry*, Final Report. EPA Contract No. 68-01-2288, PB 259 097, Pasadena, CA, Jacobs Engineering Co., June 1976.

BIBLIOGRAPHY (Continued)

SE-066 Selmeczi, Joseph G. and R. Gordon Knight, "Properties of Power Plant Waste Sludges," Paper #B-8, Presented at 3rd Int'l. Ash Utilization Symposium, Pittsburgh, PA, March 1973.

SH-418 Shaw, N. R., "Vapor Adsorption Technology for Recovery of Chlorinated Hydrocarbons and Other Solvents," Prepared for 68th Annual Meeting of the Air Pollution Control Assoc., Boston, MA, June, 1975.

SL-034 Slack, A. V. and J. M. Potts, "Disposal and Use of By-Products from Flue Gas Desulfurization Processes. Introduction and Overview." Presented at the Flue Gas Desulfurization Symposium, New Orleans, May 1973.

SL-084 Slimak, K. M., Landfill Disposal Systems. McLean, VA., TRW Inc., 1977.

ST-351 Stanford Research Institute, 1976 Directory of Chemical Producers, U.S.A., Menlo Park, California, 1976.

ST-667 Straus, M. A., Hazardous Waste Management Facilities in the United States - 1977, Publication SW-146.3, Environmental Protection Agency, Cincinnati, OH, 1977.

TI-062 Tierney, D. R. and T. W. Hughes, Source Assessment: Reclaiming of Waste Solvents, State of the Art, EPA Contract No. 68-02-1874, Monsanto Research Corporation, Dayton, OH, April 1978.

US-209 U.S. Bureau of Mines, Crude Petroleum, Petroleum Products, and Natural Gas Liquids, December, 1974, Mineral Industry Surveys, Petroleum Statement Monthly, Washington, D.C., April, 1975.

VA-203 Van Ingen, R. E. and B. N. Bastian, "Factors Affecting Waste Disposal Alternatives," Paper No. AM-76-31. Presented at the 1976 NPRA Annual Meeting, San Antonio, TX, March 1976.

VI-068 Viraraghanam, D. and R. C. Landine, "Economic Evaluation of Four Sludge Dewatering Devices," Poll. Eng. 1978 (Sept.), 55-57.

WA-412 Wachter, R. A. et. al., Study to Determine Need for Standards of Performance for New Sources of Waste Solvents and Solvent Reclaiming, EPA Contract No. 68-

BIBLIOGRAPHY (Continued)

02-1411, Task 15, Monsanto Research Corporation, Dayton, Ohio, February 1977.

WA-413 Water Pollution Control Federation, *Technical Practice Committee, Operation of Wastewater Treatment Plants*, A Manual of Practice, No. 2., Oct. 1975.

WI-197 Wisniewski, Ralph H., *Ultimate Disposal Methods of Refinery Sludges*, Pittsburgh, PA, CHEMFIX, Inc., undated.

WI-331 Witt, P. A. Jr., "Disposal of Solid Waste," *Chem. Eng*. *78*(22), 62-78, 1971.

YA-089 Yaverbaum, Lee, *Fluidized Bed Combustion of Coal and Waste Materials*. Park Ridge, NJ, Noyes Data Corp., 1977.

APPENDIX I

EVALUATIONS OF SOLID WASTE PROCESSING AND DISPOSAL TECHNIQUES

TABLE OF CONTENTS

Page

Treatment

Vacuum Filtration I-2
Pressure Filtration I-7
Centrifugation I-16
Dewatering Lagoons I-24
Aerobic Digestion I-29
Anaerobic Digestion I-35
Chemical Fixation I-43
Sand Drying Beds I-47
Wet-Air Oxidation I-53
Composting I-57
BEST/Solvent Extraction I-62

Final Disposal

Landfilling I-66
Landfarming I-71
Incineration I-75
Disposal Lagoons I-86
Disposal Wells I-88
Ocean Disposal I-90

Process/Equipment: Vacuum Filtration

Application:
Sludge Dewatering
- Raw or Digested Biological Treatment Sludges
- Slop Oil Emulsions
- Separator Sludges

Process Description: Vacuum filtration involves separation of waste solids from water at the surface of a porous filter medium under vacuum. Solids accumulate on the filter's surface while water passes through as filtrate. The filter cake is removed as the dewatered product. Although there are many variations to the basic vacuum filter, it operates by drawing a vacuum on the discharge side of a filter medium made of cloth, steel, tightly wound coil springs, etc. Often a precoat layer is applied to the filter drum to prevent oily solids residue from clogging the pores of the filter medium. The vacuum provides the driving force for filtrate flow through the filter medium. Solids in the feed are physically strained from the filtrate. To increase capacity and improve collection efficiency, precoats, flocculants, or coagulants are frequently used. Figure 1 shows a rotary vacuum filter system.

Development Status: Vacuum filters have been used by refineries for many years to dewater sludges before further processing and/or final disposal.

Performance:

Control Effectiveness: Vacuum filtration is most frequently used to dewater sludge containing 5 to 10 percent solids. Solids losses typically range from 2-10 percent. The dewatered sludge contains 15-35 wt percent solids, with 25 percent being typical.

Process Reliability:

Complexity - Skilled labor is required.

Start-up and Shutdown - Can be performed easily.

Equipment - Vacuum system, filtration unit, sludge pump, flocculant feeder and mixer.

Materials of Construction - Materials required for the aforementioned equipment.

Raw Materials - Flocculants or coagulants may be needed.

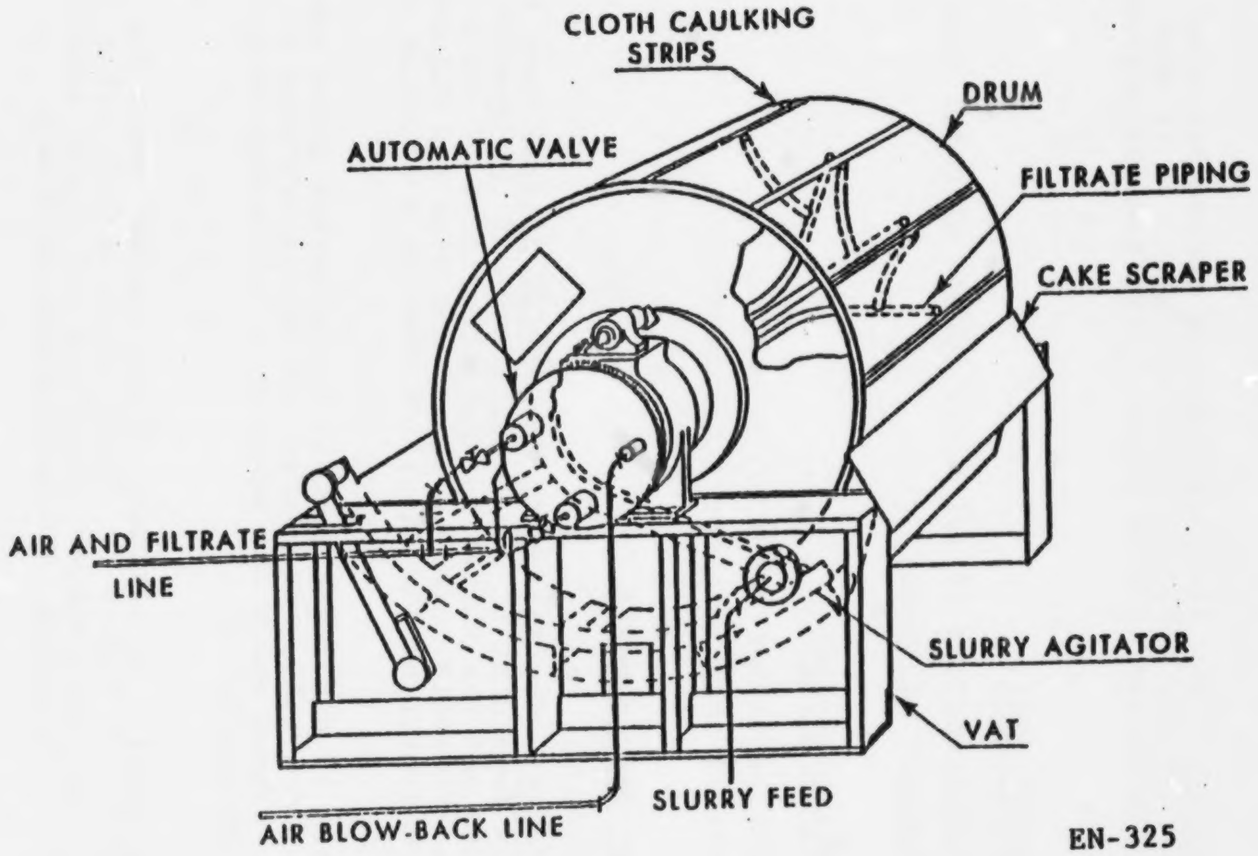

CLOTH CAULKING
STRIPS
DRUM
AUTOMATIC VALVE
FILTRATE PIPING
CAKE SCRAPER
AIR AND FILTRATE
LINE
SLURRY AGITATOR
VAT
SLURRY FEED
AIR BLOW-BACK LINE
EN-325

FIGURE 1. CUTAWAY VIEW OF A ROTARY DRUM VACUUM FILTER

Secondary Pollutants: The secondary pollutants from vacuum filtration are the filtrate and the dewatered sludge (filter cake). The filtrate is sent to a separator where oil suitable for distillation or cracking is recovered and the water layer recycled to the treatment plant. The dewatered sludge requires disposal such as landfill, landfarm, or incineration.

Applicability: This sludge processing method has wide application in dewatering refinery waste sludges. It is most suitable for low-volume streams where a high quality effluent is desired.

Process Advantages:

- Concentration of solids to reduce disposal cost
- Compact equipment

Process Disadvantages:

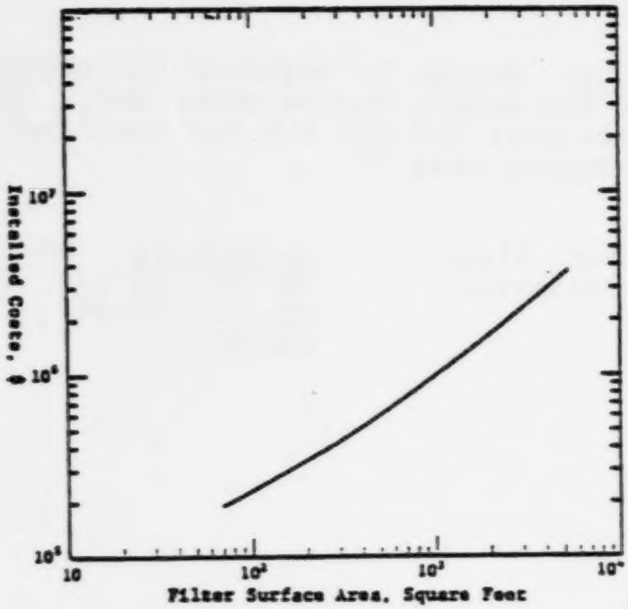
- Skilled labor required
- Use of coagulants or flocculants

Cost and Energy Requirements:

Capital Costs: Capital costs for vacuum filters vary significantly depending on the requirements of the specific application and the filtering characteristics of the solids. Costs are primarily based on the filter area and Figure 1 gives an estimate of the installed cost as a function of the area.

An estimate of the total capital costs versus plant capacity in tons of dry solids recovered per day is provided in Figure 2. These costs are based on a filtration rate of 4 lb dry solids/ft^2 hr.

Operating Costs: An estimate of the current operating costs is also shown in Figure 2. These costs include labor for operations and maintenance, chemicals for sludge conditioning prior to filtering, and maintenance materials.

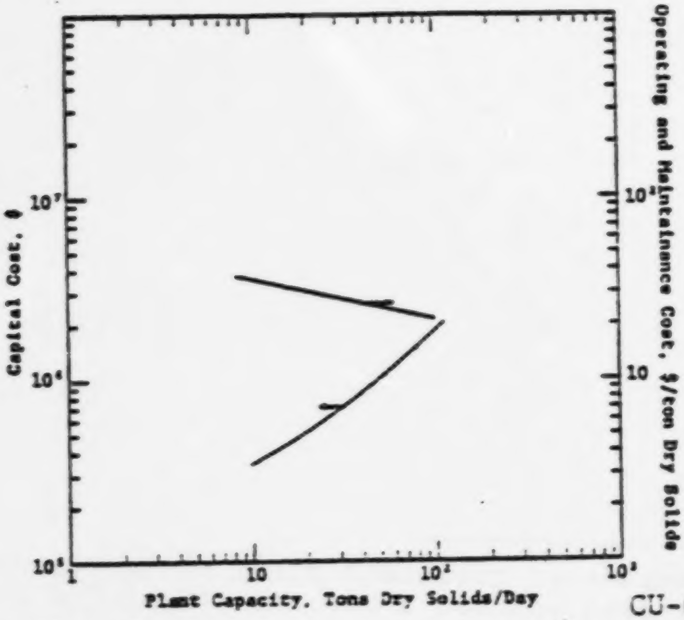


July 1977 cost index = 204.5

December 1978 cost index = 225

CU-082

FIGURE 1. VACUUM FILTRATION CAPITAL COSTS (JULY 1977)



July 1977 cost index = 204.5

December 1978 cost index = 225

CU-082

FIGURE 2. VACUUM FILTRATION CAPITAL AND O&M COSTS (JULY 1977)

Energy Requirements: Energy is required for sludge pump, flocculant feeder and mixer, vacuum pump, etc. The reported annual requirements were 340,000 kwh for one case* and 230,000 kwh for another case.**

Manufacturers or Developer: Dorr-Oliver, Eimco, Komline-Sanderson, Envirex

References: AM-046, EN-295, MA-232, PO-079, CU-082, EN-325, CU-087, AM-042, AM-062

---

*10x10^3 gal/day wastewater treatment plant design parameters for vacuum filter are feed solids, 5 percent, yield 2.8 lb/hr/ft^2, cake moisture 75 percent, and lime dose 4 percent by weight.

**10x10^3 gal/day wastewater treatment plant, design parameters for vacuum filter are feed solid 12 percent, yield 8 lb/hr ft^2, cake solids 24 percent, polyelectrolyte dose 10 lb/ton of dry solids.

Process/Equipment: Pressure Filtration Application: Sludge Dewatering

Process Description: Filtration may be defined as the removal of solid particles from a fluid by passing the fluid through a filtering medium, or septum, on which the solids are deposited. The two major categories of filtration apparatus are pressure and vacuum, which may be further classified by continuous or batch operations. This description includes continuous and batch pressure filters. The major types that find use in processing refinery wastes are:

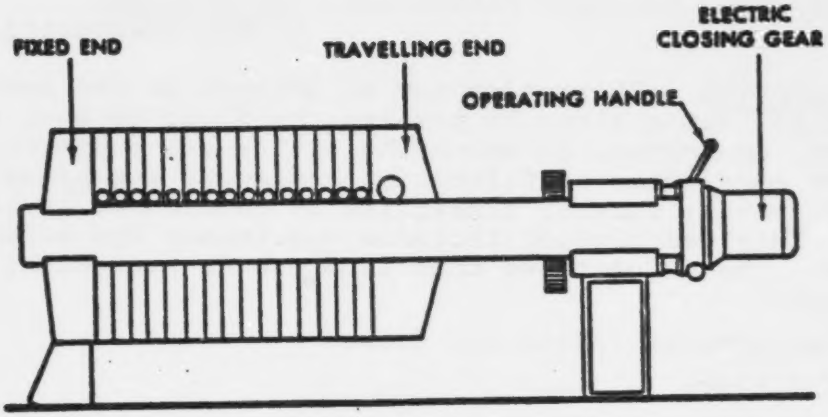
- Filter presses (plate-and-frame)
- Leaf filters
- Horizontal belt filters

The first two are discontinuous filters; the third is a continuous filter designed to compete with rotary vacuum filters. Figures 1 through 3 illustrate different views of the three different systems.

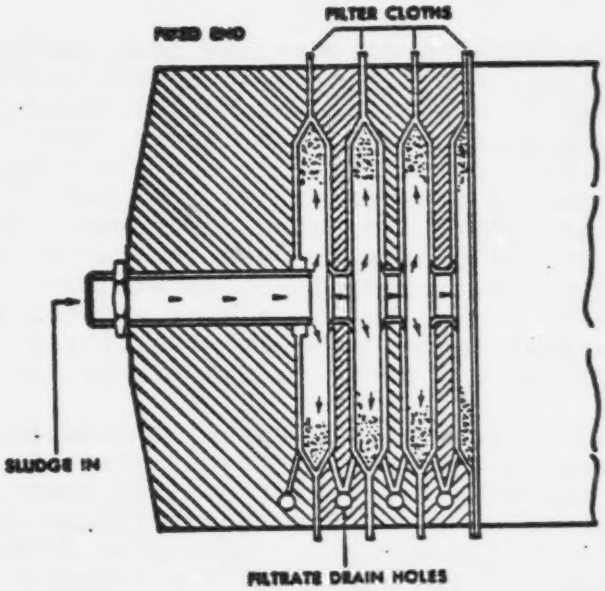
The plate-and-frame filter press, as the name implies, contains alternate solid plates, the faces of which are studded, grooved, or perforated to permit drainage, and hollow frames, in which the cake collects during filtration. The plates, most often rectangular, are covered with a fabric filter, and are hung on parallel bars. Hydraulic rams or powered screws are used to hold the plates together. Slurry is admitted to each compartment under pressures of 60 to 225 psi; liquor passes through the canvas and out a discharge pipe, leaving a wet cake of solids behind. Typical filtration times range from 1 to 3 hours, making a total cycle time of 2 to 5 hours. The most common problem with filter presses is the clogging or blinding of the pores in the filter cloth.

The horizontal leaf filter permits higher operating pressures and less labor requirements than the plate-and-frame press. However, its capital costs are much higher for a given quantity of filtration capacity. Leaves covered with fabric filter are vertically hung and inserted in a closed tank. Slurry at high pressure is admitted to the tank and allowed to filter through the noncontiguous leaves. Filtrate is drained off through a discharge tube and, after sufficient time for full caking, the tank opened and dewatered product removed. Batch and cycle times are similar to the plate-and-frame system.

In response to the high capital costs and labor expenses associated with the above discontinuous filters, many refiners have introduced the horizontal belt gravity filter press to dewater


FIXED END
TRAVELLING END
ELECTRIC
CLOSING GEAR
OPERATING HANDLE

(a) Side View

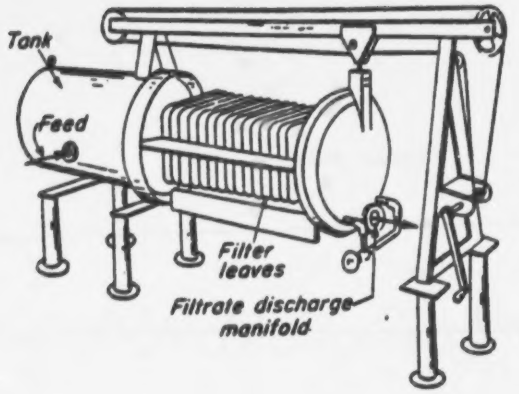

FILTER CLOTHS
FIXED END
SLUDGE IN
FILTRATE DRAIN HOLES

(b) Cutaway View

EN-325

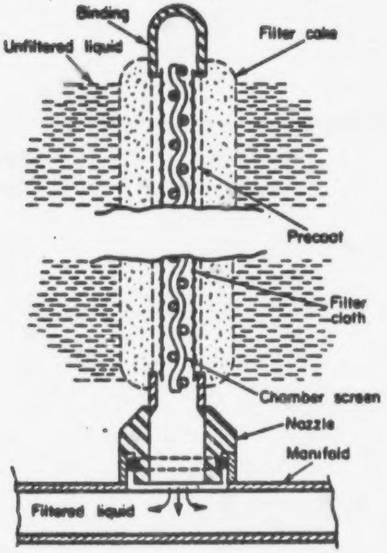
FIGURE 1

FILTER PRESS


Tank
Feed
Filter leaves
Filtrate discharge manifold

MC-389

(a) Isometric View

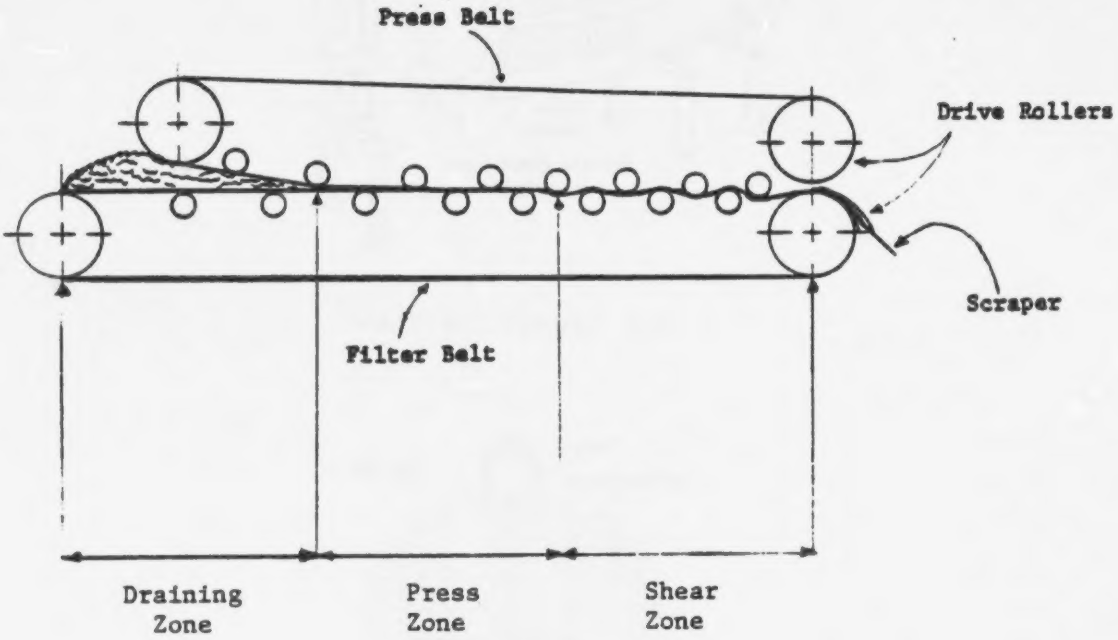

Binding
Unfiltered liquid
Filter cake
Precoat
Filter cloth
Chamber screen
Nozzle
Manifold
Filtered liquid

PE-277

(b) Cutaway View

FIGURE 2

HORIZONTAL LEAF FILTERS


Press Belt
Drive Rollers
Scraper
Filter Belt
Draining Zone
Press Zone
Shear Zone

EN-325

FIGURE 3

A SCHEMATIC OF THE GRAVITY BELT FILTER PRESS sludges. This filter consists of two continuous belts mounted on horizontal guides and rollers. Direction and speed of the two belts are identical. Three zones of varying pressures effect dewatering. In the initial draining zone, gravity is the driving force. Static pressure is applied in the pressure zone and, in the shear zone, the belt guides cause the belts to be displaced relative to each other; this generates shear forces which accomplish final dewatering. A scraper or knife blade removes dried cake. Based on suspended solids of 3 to 6 wt. percent in the feed, this friable cake contains 20 to 35 wt. percent solids, with 30 wt. percent being typical.

Development Status: Pressure filtration is a common unit operation in use for many years. Horizontal belt filters are widely used in Europe; these systems were introduced to the United States in 1970.

Performance:

Control Effectiveness: Data for the different systems is presented in the following table:

Type of System	Type of Municipal Sludge	Suspended Solids in Feed (wt %)	Cake Solids (wt %)
Filter press	Raw primary	5-10	50
	Digested	6-10	50
	EAS	<5	50
Horizontal leaf	Raw primary	3-8	50
	Digested or EAS	(Not Available)	
Horizontal gravity belt	Raw primary	3-6	29-35
	Digested	4-7	39-44
	Digested with EAS	10	38

Sources: EN-325, PE-277, AS-070

Process Reliability:

Complexity - Skilled labor is required.

Start-up and Shutdown - Again, skilled labor is mandatory for batchwise operation.

Equipment - Pumps, filtration apparatus, handling equipment for filter aids.

Materials of Construction - No special materials required.

Raw Materials - Filter aids such as flocculants or coagulants may be required. Polymers are the most widely used chemical additive for belt filter presses; $FeCl_3$ and CaO are the usual additives for plate-and-frame presses.

Secondary Pollutants: Filtrate is sent to an oil/water separation unit before recycling to the wastewater treatment facility. Dewatered filter cake must be disposed of in a landfill or another environmentally acceptable manner.

Applicability: The use of pressure filters is applicable to most refinery sludges. Slurries of fines are also amenable to this treatment technique.

Process Advantages:

- Concentration of solids to reduce disposal cost.
- Compact equipment/low floor space requirements.
- No complex equipment or processing.
- Eliminates high land requirements.
- High solids capture.

Process Disadvantages:

Batch filters:

- Skilled labor required.
- Filtrate and cake require further treatment.
- High maintenance usually required.
- Pretreatment chemical conditioning often required.

Horizontal continuous gravity belt filters:

- Lower solids cake than batch filters.
- Filtrate and cake require further treatment.
- Pretreatment chemical conditioning required.

Costs and Energy Requirements:

Capital Costs: Capital costs vary widely depending on the filtration characteristics of the sludge or slurry, the materials of construction required, the amount of auxiliary equipment required, and the filter capacity. Tables 1 and 2 show purchased cost data for batch filters.

Operating Costs: Table 3 compares capital and operating costs for a proposed municipal sludge dewatering system.

Energy Requirements: For above system:

	Filter Press	Belt Filter Press
Power	14 kwh/ton dry solids	7 hp
Labor	20 hr/wk	7 hr/wk
Chemicals	.13 ton/ton dry solids	5 lb/ton dry solids

Manufacturers or Developer: Batch filters: Numerous. Belt filter presses: Ashbrook Simon Hartley, Tait-Andritz, Parkson Corp., Ralph B. Carter Co.

References: MC-389, PE-065, PE-277, EN-325, AS-070, VI-068, AM-042, CU-082

TABLE 1

PURCHASED COST OF PLATE-AND-FRAME FILTER PRESS (DECEMBER 1978 DOLLARS)

Type of Filter and Material	Filter Area, Ft^2					
	10	20	40	60	80	100
Plate-and-Frame						
CF-8M stainless steel	$1,650	$2,950	$5,300	$7,450	$9,400	$11,500
PVC-coated iron	$1,550	$2,360	$3,630	$4,600	$5,450	$ 6,300
Cast iron	---	$1,150	$1,800	$2,320	$2,800	$ 3,200

Source: PE-065.

TABLE 2

PURCHASED COST OF HORIZONTAL LEAF FILTERS (DECEMBER 1978 DOLLARS)

Type of Filter and Material	Filter Area, Ft^2					
	2	5	10	20	30	40
Horizontal Leaf Filter						
304 stainless steel	$9,900	$16,000	$21,800	$28,800	$34,000	$37,800
Mild steel	$4,500	$ 7,780	$11,000	$15,500	$18,400	$20,800

Source: PE-065.

TABLE 3

COMPARISON OF COSTS FOR TWO FILTER SYSTEMS

	Filter Press	Belt Filter Press
Capital Cost		
Equipment[1]	117,650	101,000
Installation[2]	23,120	10,000
Total	140,770	111,000
Annual O&M Cost		
Operator Wages[3]	8,400	2,900
Power[4]	500	400
Chemicals[5]	39,600	10,700
Maintenance & Repair[6]	3,800	3,300
Sludge Transport[7]	9,700	12,800
Total	62,000	30,100
Amortized Capital & Interest Per Year[8]	22,900	18,000
Total Annual Cost	84,900	48,100
Total Cost Per Ton of Dry Solids[9]	80.1	45.4

Basis: 5,800 lb dry solids treated per day.

NOTES: [1] - Costs include chemical mix tank, chemical feed and sludge pumps and accessories; costs also include taxes and freight.

[2] - Installation cost at 20 percent of equipment for filter press; 12 percent of equipment for belt filter press.

[3] - Wages - $8/hr.

[4] - Power @ 3¢/kwh.

[5] - Dry $FeCl_3$ @ $505/ton and dry CaO @ $60/ton for filter press; polymer @ $2/lb of polymer for belt filter press.

[6] - M&R @ 4 percent of equipment cost.

[7] - Cake solids - 33 percent for filter press; 25 percent for horizontal belt filter with transport cost @ .15/ton-mile.

[8] - Amortization of 10 years at 10 percent interest - CRF = .16275.

[9] - Dry solids - 1060 ton/year.

Source: VI-068.

Process/Equipment: Centrifuge Application: Sludge Dewatering

Process Description: Centrifugation is a mechanical process using centrifugal force to speed up the sedimentation rate of sludge solid particles. A sludge is pumped into the centrifuge which is essentially a rotating drum where centrifugal forces act to hold the solids against the walls while the water stream is removed. The dewatered sludge can be removed from the centrifuge either as a continuous stream or in a batch manner. There are four types of centrifuges:

- Countercurrent solid bowl conveyor centrifuge.
- Continuous concurrent solid bowl conveyor centrifuge.
- Basket centrifuge.
- Disc centrifuge.

Figures 1 through 4 show the various types of centrifuges.

Development Status: Centrifuges of various types have been employed for solid-liquid separation processes in refineries for many decades.

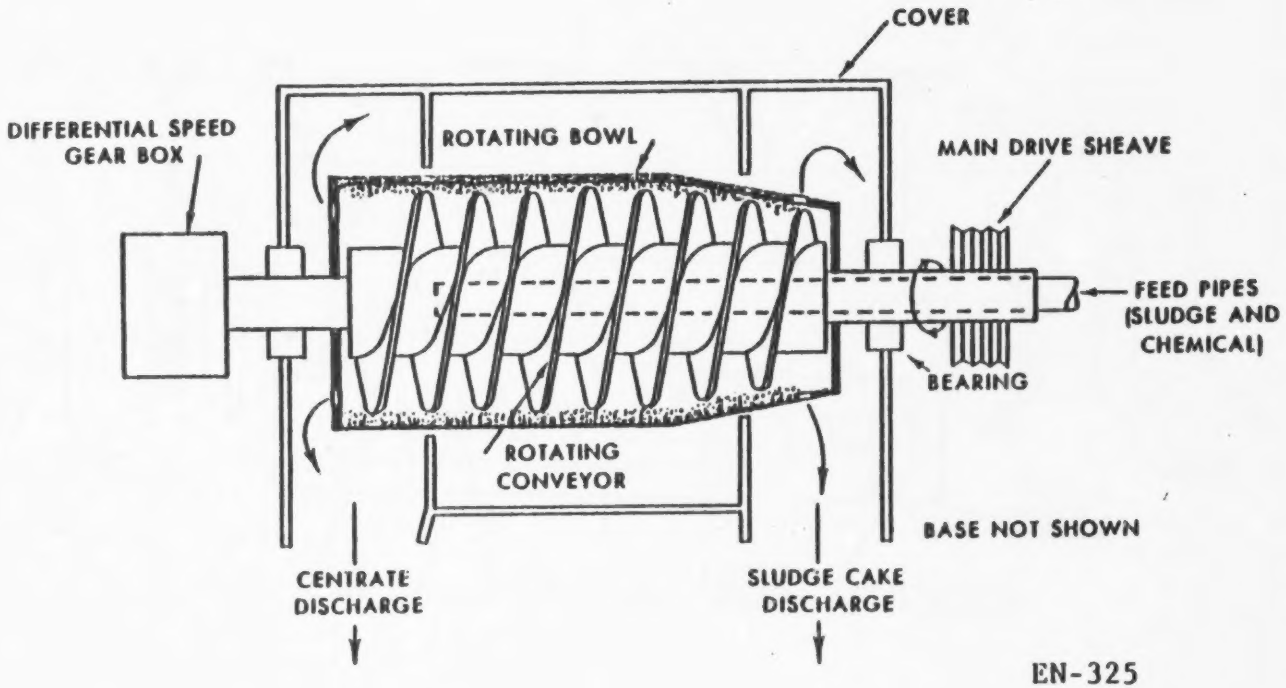
Performance:

Control Effectiveness: Sludges can be dewatered to 20 to 40 percent solids. With batch operation and long residence times, this may be increased slightly. The effectiveness in dewatering sludge is highly dependent on the physical properties of the sludge, especially the particle morphology. Industrial sludges such as limestone scrubber sludges can be dewatered up to 50-60 weight percent solids. Table 1 presents typical data which can be expected with the solid bowl configuration of various organic sludges.

Process Reliability:

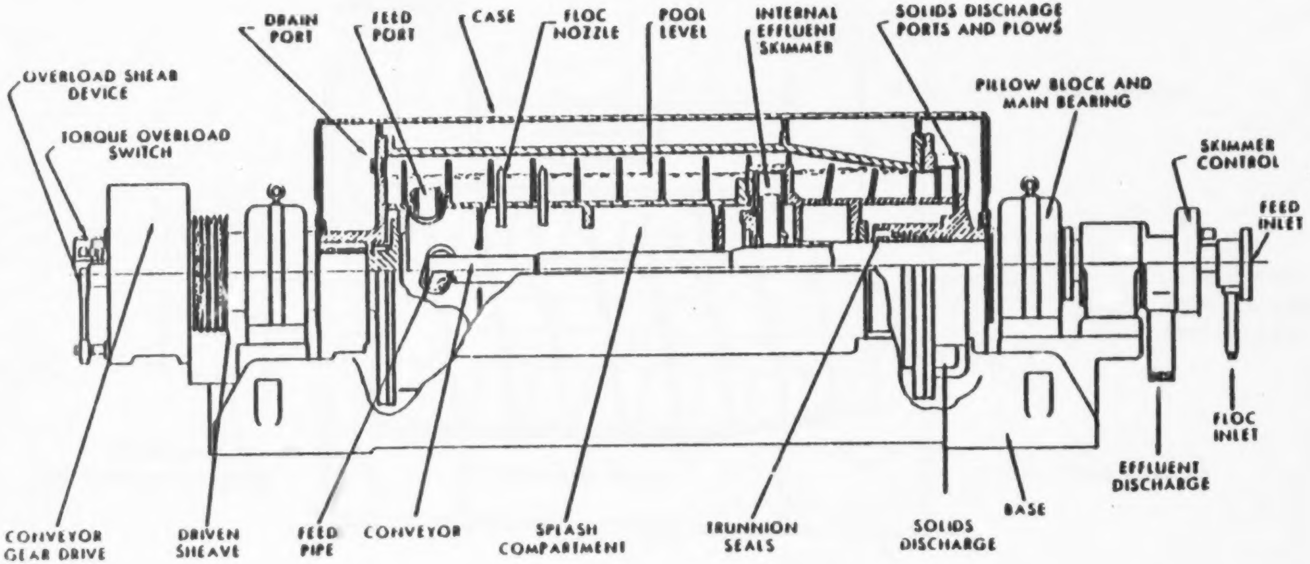
Complexity - Moderately simple process; however, operates with variable success depending on sludge properties. Skilled labor is generally required.

Start-up and Shutdown - Simple.


COVER
DIFFERENTIAL SPEED GEAR BOX
ROTATING BOWL
MAIN DRIVE SHEAVE
FEED PIPES (SLUDGE AND CHEMICAL)
BEARING
ROTATING CONVEYOR
BASE NOT SHOWN
CENTRATE DISCHARGE
SLUDGE CAKE DISCHARGE

EN-325

FIGURE 1. CONTINUOUS COUNTERCURRENT SOLID BOWL CONVEYOR DISCHARGE CENTRIFUGE


DRAIN PORT
FEED PORT
CASE
FLOC NOZZLE
POOL LEVEL
INTERNAL EFFLUENT SKIMMER
SOLIDS DISCHARGE PORTS AND PLOWS
OVERLOAD SHEAR DEVICE
TORQUE OVERLOAD SWITCH
PILLOW BLOCK AND MAIN BEARING
SKIMMER CONTROL
FEED INLET
FLOC INLET
EFFLUENT DISCHARGE
BASE
CONVEYOR GEAR DRIVE
DRIVEN SHEAVE
FEED PIPE
CONVEYOR
SPLASH COMPARTMENT
TRUNNION SEALS
SOLIDS DISCHARGE

EN-325

FIGURE 2. CROSS SECTION OF CONCURRENT FLOW SOLID BOWL CENTRIFUGE

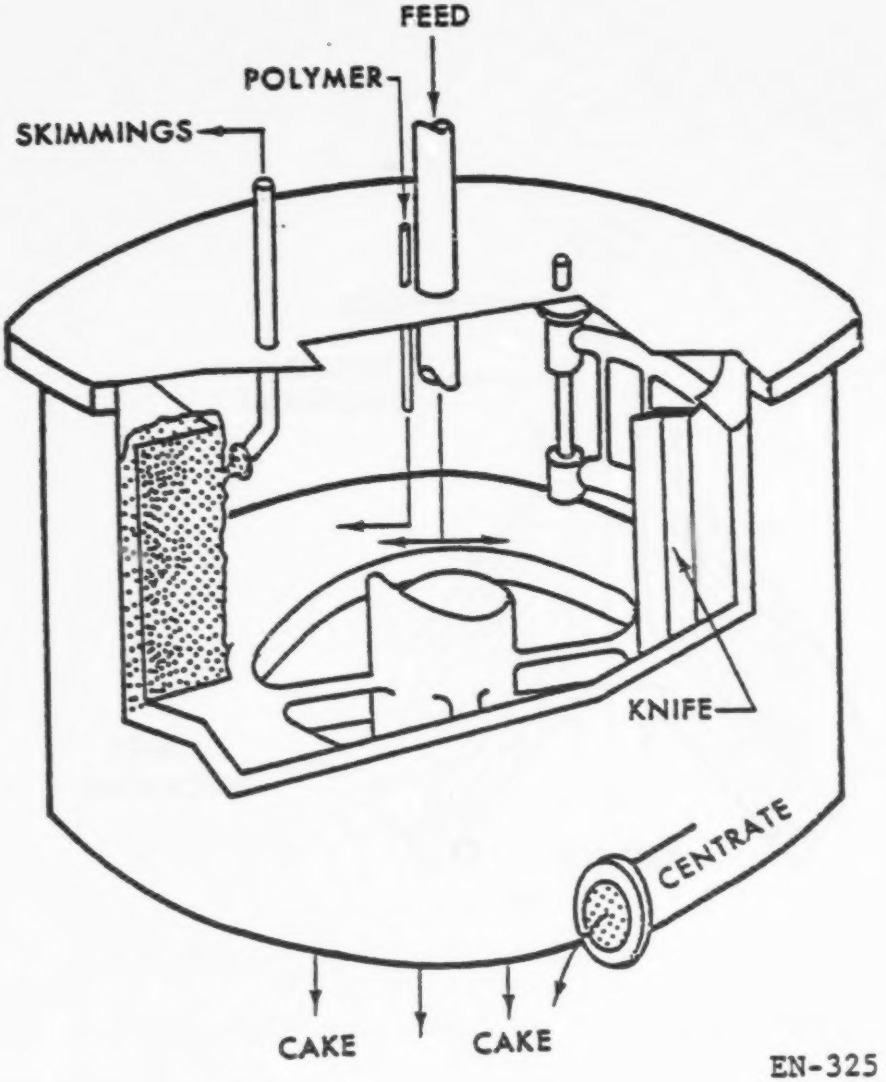
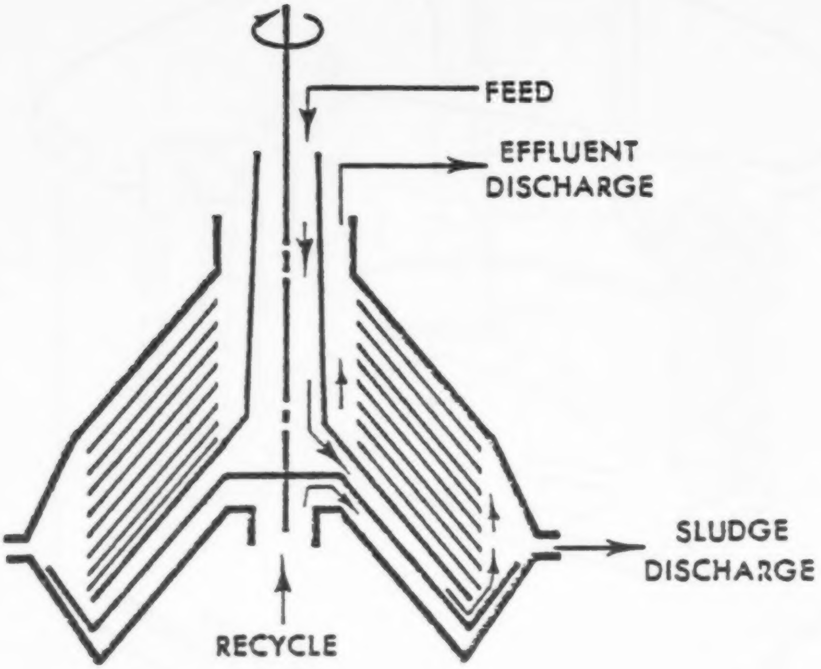

FEED
POLYMER
SKIMMINGS
KNIFE
CENTRATE
CAKE
CAKE
EN-325

FIGURE 3. SCHEMATIC DIAGRAM OF A BASKET CENTRIFUGE


FEED
EFFLUENT
DISCHARGE
SLUDGE
DISCHARGE
RECYCLE

EN-325

FIGURE 4. DISC TYPE CENTRIFUGE

TABLE 1

TYPICAL SOLID BOWL CENTRIFUGE PERFORMANCE

	Sludge Cake Characteristics		
Wastewater Sludge Type	Solids Percent	Solids Recovery Percent	Chemical Addition
Raw or Digested Primary	28-35	70-90	no
Raw or Digested Primary, Plus Trickling Filter Humus	20-30	80-95	yes
Raw or Digested Primary, Plus Activated Sludge	15-30	80-95	yes

EN-325

Equipment - Equipment required includes centrifuge, sludge pump, and flocculant feeding systems. The high-speed equipment is relatively expensive but eliminates the need for bulky equipment and floor space. Proper balancing of the rotating bowls and durable bearings is essential in order to minimize relatively high maintenance costs.

Materials of Construction - No special materials of construction are usually required. When a sludge contains abrasives, special materials may be required for internal parts of the machine.

Raw Materials - Flocculants are almost always needed to improve solid capture.

Secondary Pollutants: The concentrated solids or sludges represent a secondary waste that must be disposed. The centrate is generally sent back to the treatment plant.

Applicability: The principal application of this treatment method in petroleum refineries is the separation of solids from an oil/water/solids slurry.

Process Advantages:

- Solids concentration.
- Compact equipment.
- High throughput.

Process Disadvantages:

- Skilled labor.
- Energy costs.
- Maintenance costs.

Costs and Energy Requirements:

Costs: Listed below are capital and operating and maintenance costs for one centrifuge which is designed to handle 40 gpm of 5 wt percent municipal sludge. The sludge is dewatered to 40 wt percent solids. A capacity factor of 80 percent was assumed.

Installed Capital Costs	$313,600 (December 1978)
Operating and Maintenance Costs	$135,000/year (December 1978)

Energy Requirements: The major energy consumer for the above centrifuge is a 30 h.p. electric motor.

Manufacturers or Developer: Numerous

References: AM-042, AM-046,
EN-295, MA-232, PA-193,
PE-030, RO-423, SE-066,
SL-034, EN-325, CR-154

Process/Equipment: Dewatering Lagoons (Evaporation Ponds) Application: Sludge Dewatering

Process Description: This process is similar to the evaporation pond process described in the ultimate disposal subsection of this report, except that solids in a dewatering lagoon are periodically dredged from the lagoon. This technique is also similar to the sand drying bed -- the only differences being the lack of filtration media and underdrains. Lagooning is included in this subsection because it is the most common refinery practice for sludge dewatering. Both solar energy and gravity are used to dewater the sludge. The solar energy flux on the lagoon surface causes water to evaporate; this concentrates the suspended solids. Often, though, dewatering due to gravity settling is more effective in separating the two phases. After sufficient accumulation of the solids occurs at the lagoon bottom, they must be dredged and further processed.

The design of dewatering lagoons is affected by the net evaporation rate, i.e., the gross evaporation rate minus rainfall. Geological characteristics of the area are also a major factor. If the soil is highly permeable, the lagoon must be lined with clay or a synthetic liner. In some areas, state or local regulations may prohibit dewatering lagoons. Lagoons can be constructed by excavating a hole, typically 8 to 15 feet deep; enclosing an area with dikes; building a dam or a combination of the above.

Development Status: Dewatering lagoons have been used for many decades by the petroleum refining industry for the disposal of refinery sludges.

Performance:

Control Effectiveness: All solid waste streams that require dewatering can potentially be dewatered by lagoons, but land availability and evaporation rate may limit high flow rate streams from being discharged to a lagoon. The major limitations to the control effectiveness of drying lagoons even in arid regions is the problem of seepage of toxic components into groundwater supplies. Even with the most carefully designed lined dewatering lagoon, there is always the possibility of rupture of the lining and subsequent leakage. There is also the question of the effectiveness of lagoon liners. Chemical reactions of the contents of the lagoon with the clay liners has been observed which increases liner permeability and thus the possibility of groundwater contamination. The volatile organic compounds are evaporated.

Process Reliability:

Complexity - Simple process.

Start-up and Shutdown - Simple.

Equipment - No special or unique process equipment required.

Materials of Construction - Clay or synthetic liners may be needed.

Raw Materials - No raw materials required.

Secondary Pollutants: These ponds are seldom designed for environmental compatability. Only if adequate lining and continued monitoring are provided does this technique provide sufficient water and land protection. Even then, evaporation of volatile organic compounds occurs. These air emissions, coupled with a history of ineffective leachate control, have elicited heavy regulation from the government which curtails the use of dewatering lagoons.

Applicability: Have been demonstrated in refineries and chemical process industries.

Costs and Energy Requirements:

Costs: In Figures 1 and 2, capital and operating costs of dewatering lagoons are shown as a function of water rate to the lagoon with the effective net evaporation rate as a parameter. The effective net evaporation rate is less than the net evaporation rate due to the reduction of the water vapor pressure that is caused by the dissolved salts in the water in dewatering lagoons. The capital cost figure is based on a 4 foot high dike with a 27 foot dike base, and includes liner and land costs. The cost of excavation can range from \$2 to \$6/cu yd depending upon the type of land to be excavated. Liner costs can range from \$0.20 to \$0.40/ft^2 depending upon the type and thickness of liner used. Land costs can range anywhere from \$200/acre to \$10,000/acre or more.

Energy Requirements: The major energy requirement for dewatering lagoons is for pumping wastewater to the lagoon.

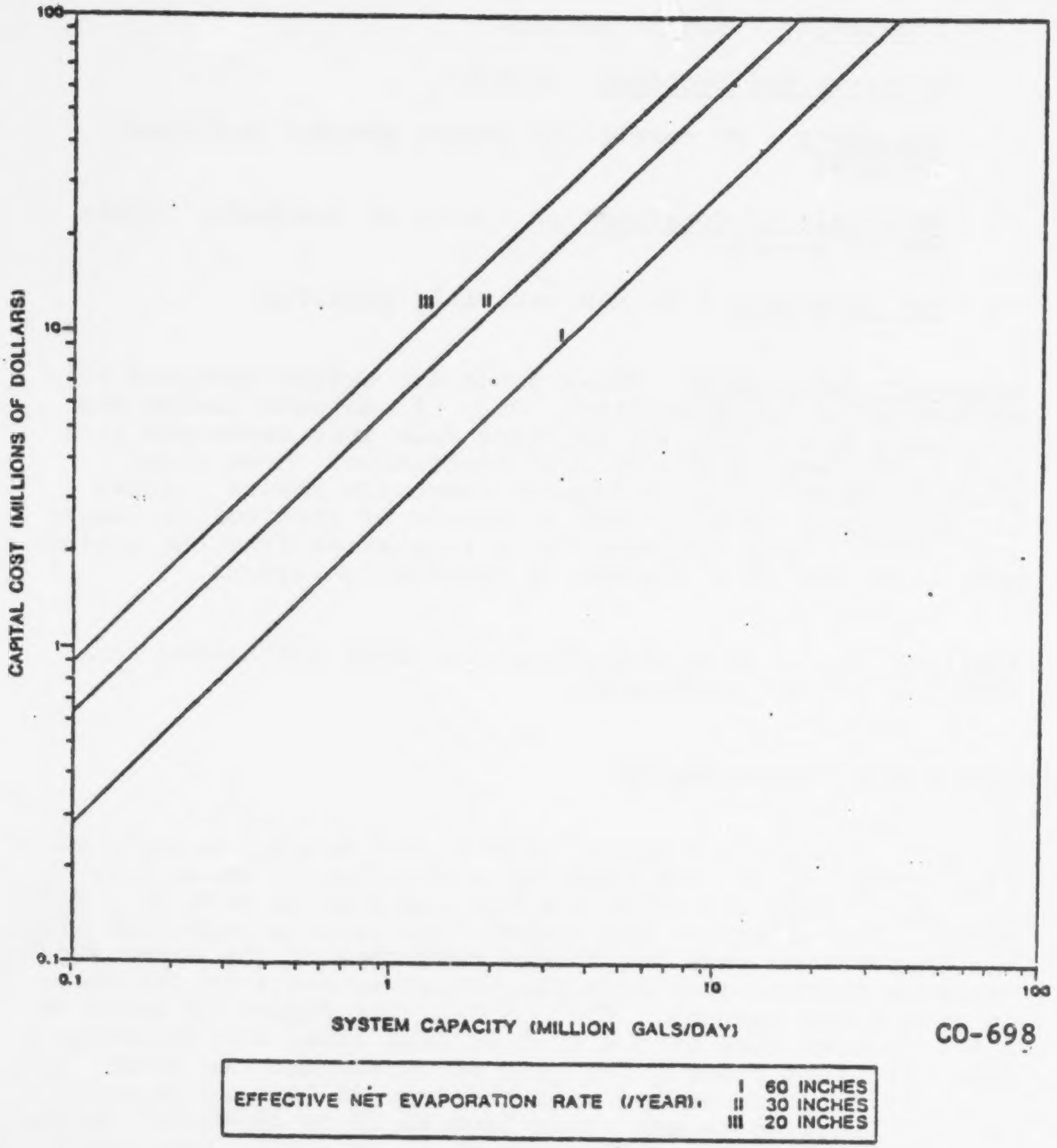
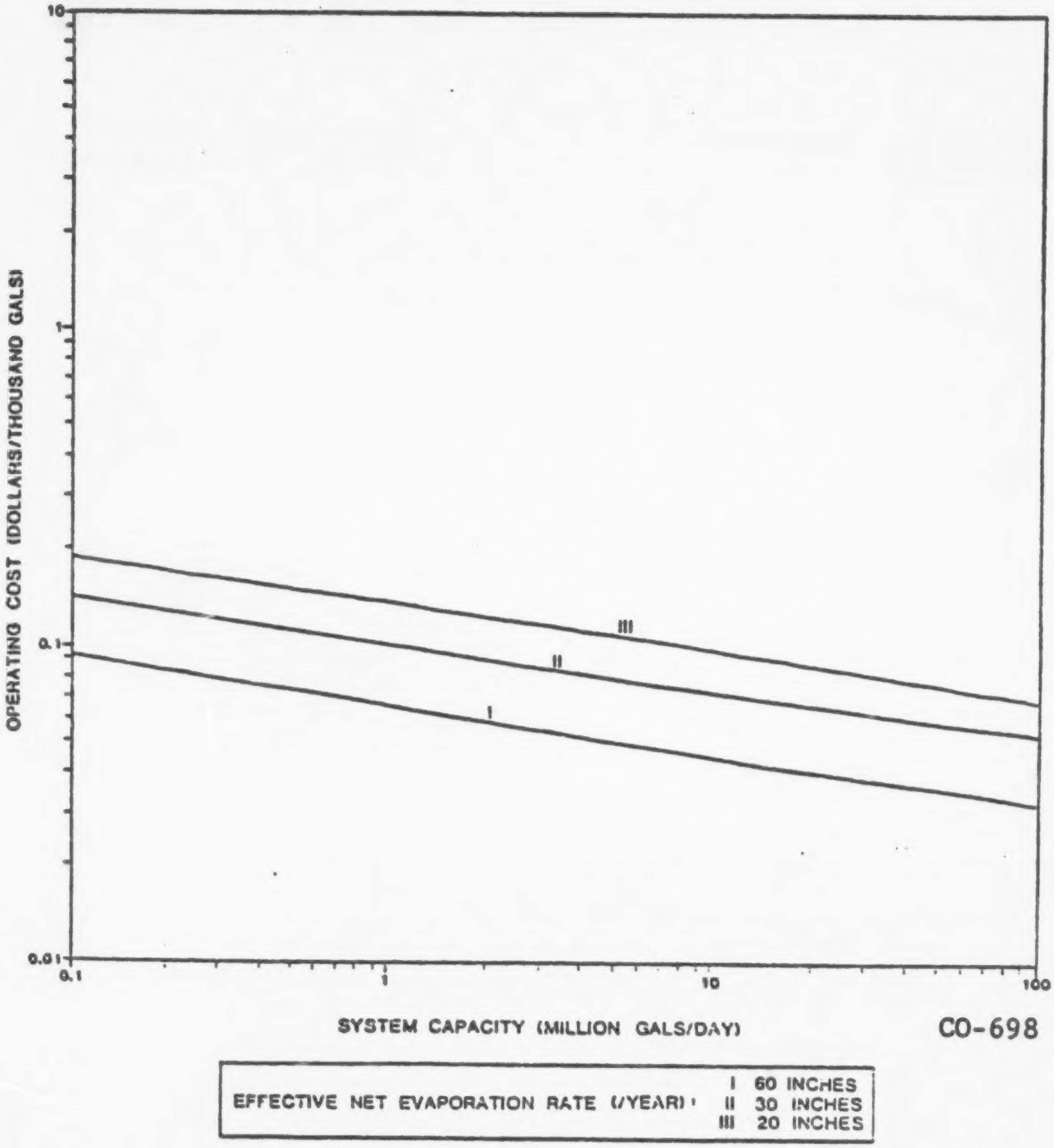


FIGURE 1. CAPITAL COSTS FOR DEWATERING LAGOONS



CO-698

FIGURE 2. DEWATERING LAGOON OPERATING COSTS

The energy requirement for pumping 1000 gallons a distance of 1000 feet is about 0.5 kwhr (based upon a 5 ft/sec flow velocity).

Manufacturers or Developer: Numerous.

References: AM-042, CO-698, EN-818, RO-423

Process/Equipment: Aerobic Digestion **Application**:
Waste Biological Sludge
Volume Reduction and
Stabilization

Process Description: Aerobic digestion is similar to the activated sludge process. The primary difference is a change in respiration type due to extended detention times in the digestors. As the available dissolved organics are depleted, the bacteria begin to consume themselves (endogenous respiration) to obtain the energy required in cell metabolism. The fundamental concept is that biological self-destruction occurs at a faster rate than microbial growth.

Figure 1 shows a schematic of an aerobic digestion system. Waste biological sludge is admitted to the tank where it undergoes aeration and mixing. Bacteria consume the organic nutrients present before metabolizing themselves. Supernatant is drawn off, clarified, and recycled to the head of the treatment plant. Thickened sludge is drained and dewatered or sent immediately to a landfarming or landfilling site.

The important process parameters in conventional air aerobic digestion are:

- Oxygen requirements
- Detention time
- Sludge age
- Temperature
- Biodegradable volatile solids level
- pH

High-rate volatile solids reduction occurs in the first 10-12 days, typically with 35 percent to 45 percent of the volatile suspended solids (VSS) removed. Fifteen days of detention time are commonly provided for stabilization of excess biological sludges. Loadings will normally vary from .1 to .2 lb VSS/ft^3 day. If the influent sludge has a VSS content of greater than 3 percent, an oxygen-rich stream must be provided which has a higher oxygen fraction than atmospheric air. Figure 2 depicts a typical continuous flow aerobic digester.

Development Status: Aerobic digestion has been used for many years in municipal wastewater treatment systems. It has also been extensively used in petroleum refinery excess activated sludge stabilization.

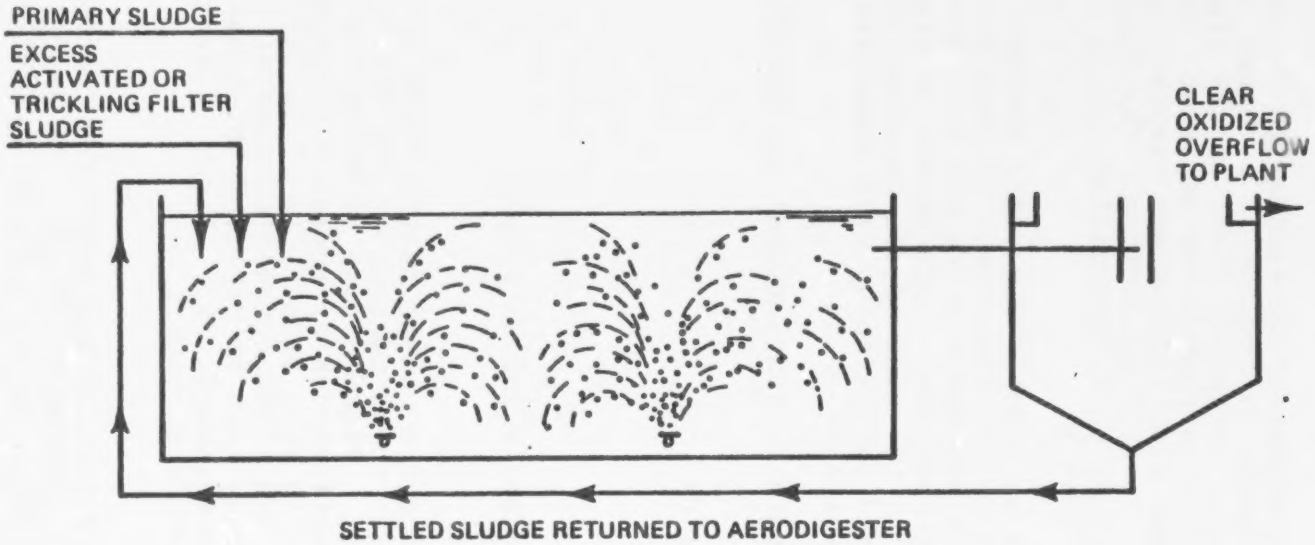
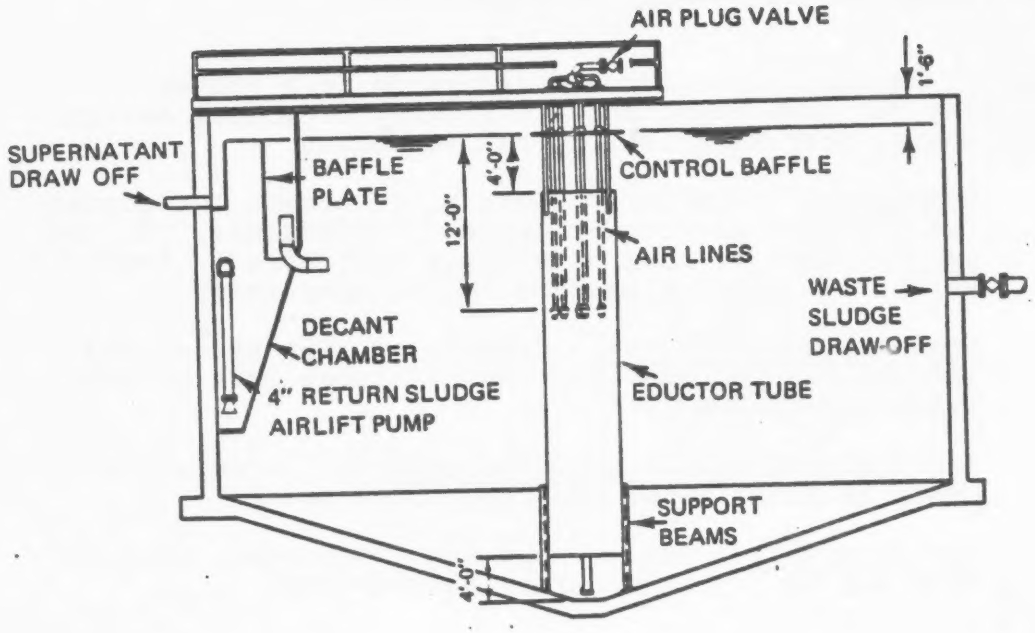

PRIMARY SLUDGE
EXCESS ACTIVATED OR TRICKLING FILTER SLUDGE
CLEAR OXIDIZED OVERFLOW TO PLANT
SETTLED SLUDGE RETURNED TO AERODIGESTER

FIGURE 1

EN-325

A SCHEMATIC OF AN AEROBIC DIGESTION SYSTEM


AIR PLUG VALVE
1'-6"
SUPERNATANT DRAW OFF
BAFFLE PLATE
4'-0"
12'-0"
CONTROL BAFFLE
AIR LINES
WASTE SLUDGE DRAW-OFF
DECANT CHAMBER
4" RETURN SLUDGE AIRLIFT PUMP
EDUCTOR TUBE
SUPPORT BEAMS
4'-0"

EN-325

FIGURE 2

A TYPICAL CIRCULAR (CONTINUOUS FLOW) AEROBIC DIGESTER

Performance:

Control Effectiveness: Total VSS removal ranges from 40 to 50 wt percent at fifteen days detention time. The recycled supernatant typically contains 500 mg/ℓ of BOD_5, 2600 mg/ℓ of COD, and suspended solids of 3400 mg/ℓ The sludge is essentially pathogen-free.

Process Reliability: Aerobic digestion is a proven process; yet some questions still exist regarding design parameters, process kinetics, and economics.

Complexity - Similar to most biotreatment techniques, this process is complex because temperature, pH, and oxygen transfer must be closely controlled. Required analytical monitoring adds to the complexity.

Start-up and Shutdown: Seeding of this system and initial loading and draining of sludge must be carefully undertaken.

Equipment/Materials of Construction: Circular concrete or steel tanks are most often used.

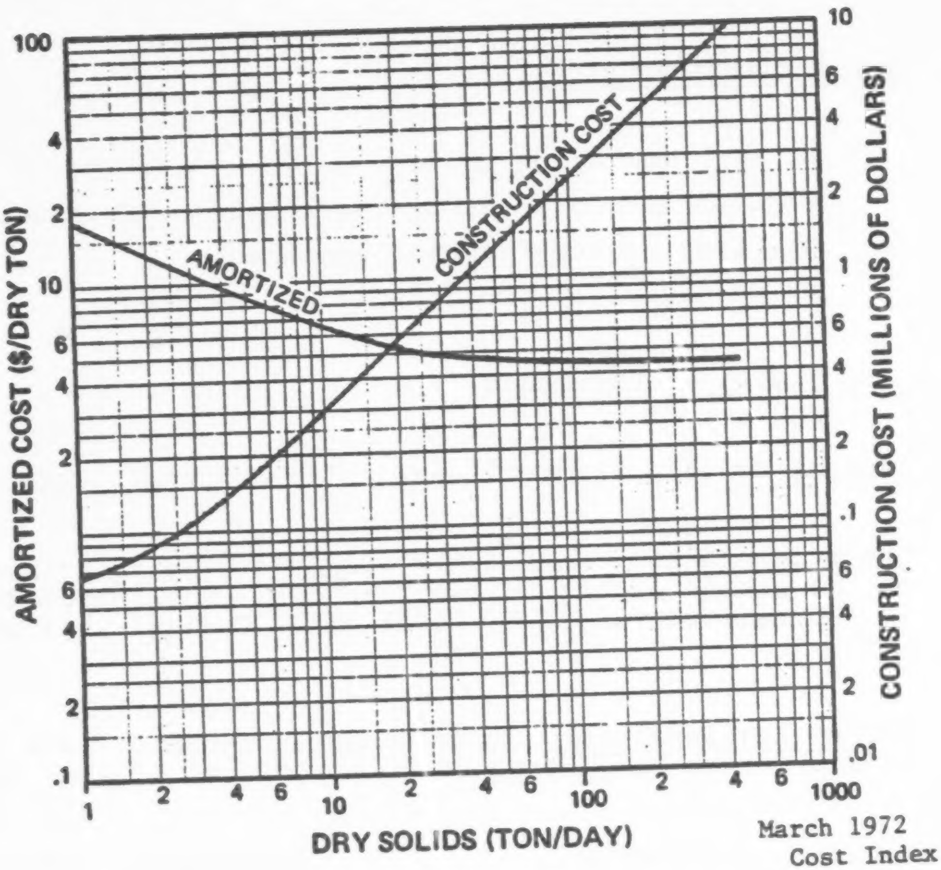
Raw Materials: Seed sludge and air/oxygen; auxiliary heat may be required during cold months.

Secondary Pollutants: The supernatant contains low amounts of BOD, total P, and kjeldahl N; it is high in suspended solids. Sludge must be disposed of in a landfarm or landfill. Odors may require control in high wind areas.

Applicability: Aerobic digestion has been applied by a significant number of refineries in treatment of waste biosludges.

Process Advantages:

- Low capital costs
- No generation of significant odors
- Reduces pathogens to low levels
- Low BOD concentrations in supernatant
- Production of an easily dewatered, biologically stable end product



March 1972
Cost Index - 136.2

December 1978
Cost Index = 225.0

NOTES:

1. Minneapolis. Mar., 1972. ENR Construction Cost Index of 1827.
2. Amortization at 7% for 20 years.
3. Influent sludge of 38% primary and 62% waste activated sludge with a solids content of 3.5%.
4. 20 day volumetric displacement time.
b. Souce: EPA Cost and Manpower Report and Stanley Consultants.

FIGURE 3

CAPITAL COSTS OF AN AEROBIC DIGESTER

- Recovery of fertilizer values
- Fewer operational problems than anaerobic digestion.

Process Disadvantages:

- High operating costs
- Less developed design parameters and kinetics
- Close process control required
- No useful by-products, e.g., methane

Costs and Energy Requirements:

Capital Costs: Figure 3 depicts the capital costs.

Operating Costs: These vary widely depending primarily on the nature of the influent sludge. A value of $3.90/yr lb BOD removed was given for a small Pennsylvania municipality.

Energy Requirements: Sludge pumps and heaters are required. Aerator costs range from 20-40 kw/1000 m^3 of tank volume.

Manufacturer or Developers: Numerous.

References: EN-325, ME-294, WA-413

Process/Equipment: Anaerobic Digestors

Application: Waste Biosludge

Process Description: Anaerobic digestion is used to stabilize sludge, particularly in domestic applications. In the absence of oxygen, the faculative and anaerobic bacteria continue to grow and digest the organic matter. This digestion consists of two stages:

1) Hydrolysis of high-molecular-weight organics and conversion to organic acids.
2) Gasification of the organic acids to methane and carbon dioxide.

The standard rate and high rate systems are the two main digestion processes employed. Schematics of the processes as well as their operating criteria are given in Figure 1.

In practice, four types of systems have evolved from the two basic digestion modes. They are:

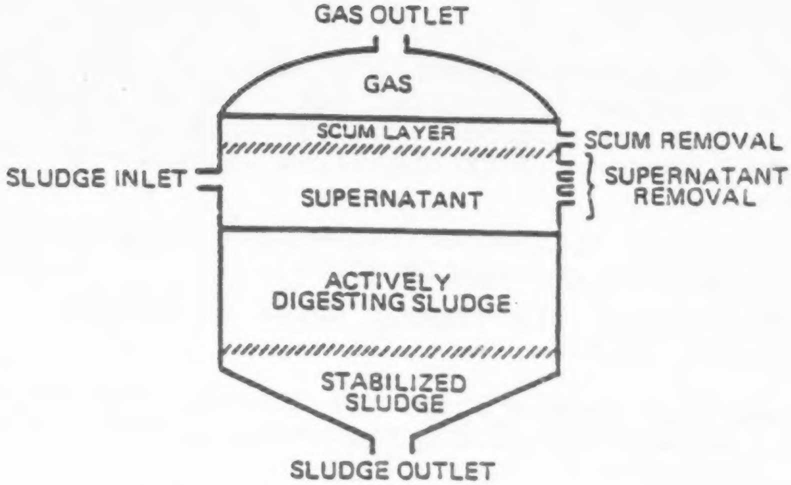
1) Standard Rate Digestion-One Stage
2) High Rate Digestion-One Stage
3) Two-Stage Digestion (Figure 2)
4) Anaerobic Contact Process (Figure 3)

Generally, the organic loading for an anaerobic system is 2-3 times greater than that for aerobic systems. However, overloading of the anaerobic system can drop the pH to toxic levels. The pH control is therefore very critical and should be maintained in the range from 6.2 - 7.5 in the anaerobic digestor.

Development Status: This process is commercially proven, and is available through numerous wastewater engineering contractors.

Performance:

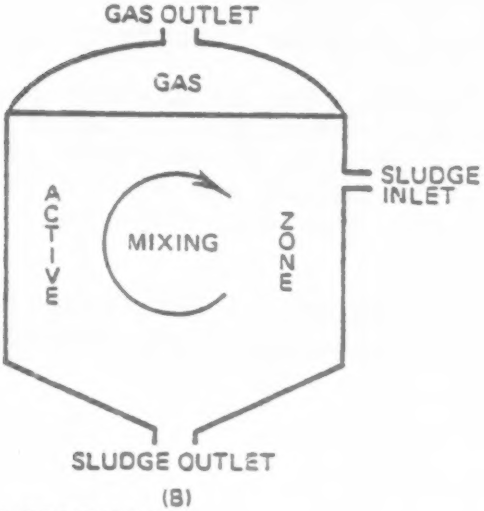
Control Effectiveness: Anaerobic digestors typically reduce organic solids 50 percent by weight.


GAS OUTLET
GAS
SCUM LAYER
SCUM REMOVAL
SLUDGE INLET
SUPERNATANT
SUPERNATANT REMOVAL
ACTIVELY DIGESTING SLUDGE
STABILIZED SLUDGE
SLUDGE OUTLET

(A)

STANDARD RATE DIGESTION

1. UNHEATED
2. DETENTION TIME 30 – 60 DAYS
3. LOADING 0.03 – 0.10 lb. VSS/cu. ft./day
4. INTERMITTENT FEEDING AND WITHDRAWAL
5. STRATIFICATION


GAS OUTLET
GAS
SLUDGE INLET
ACTIVE
MIXING
ZONE
SLUDGE OUTLET

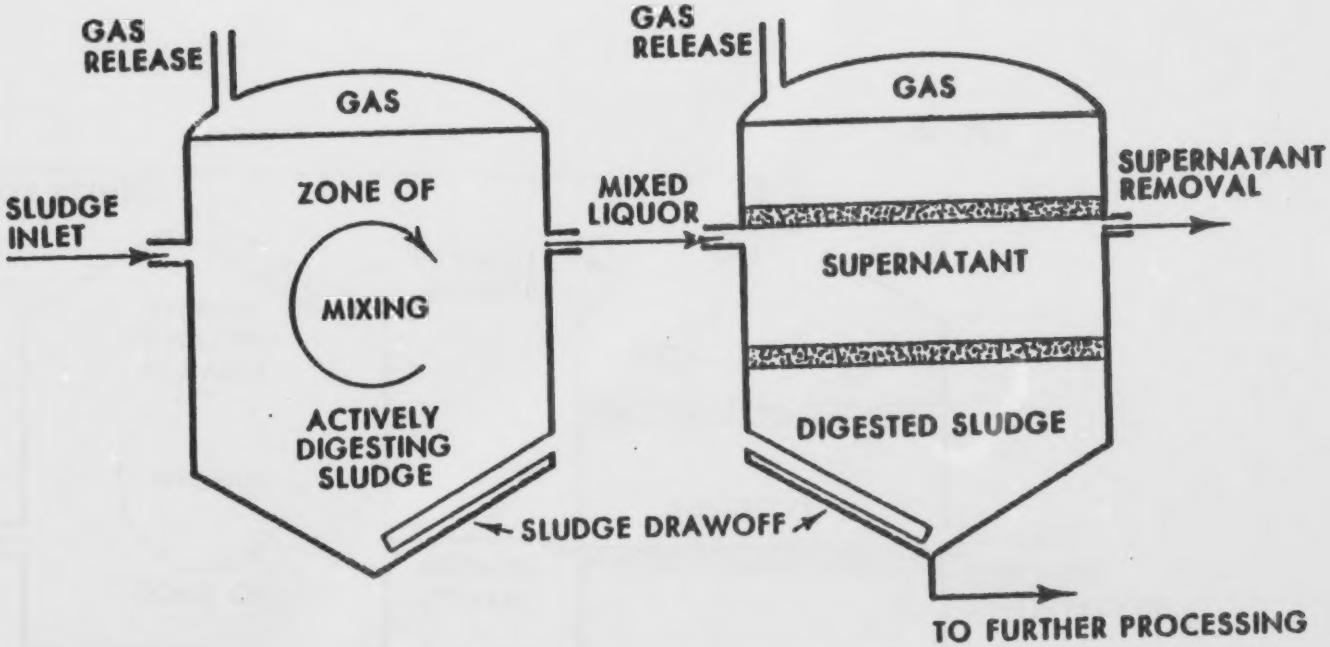
(B)

HIGH RATE DIGESTION

1. HEATED TO 85° – 95° F
2. DETENTION TIME 15 DAYS OR LESS
3. LOADING 0.10 – 0.50 lb. VSS/cu. ft./day
4. CONTINUOUS OR INTERMITTENT FEEDING AND WITHDRAWAL
5. HOMOGENEITY

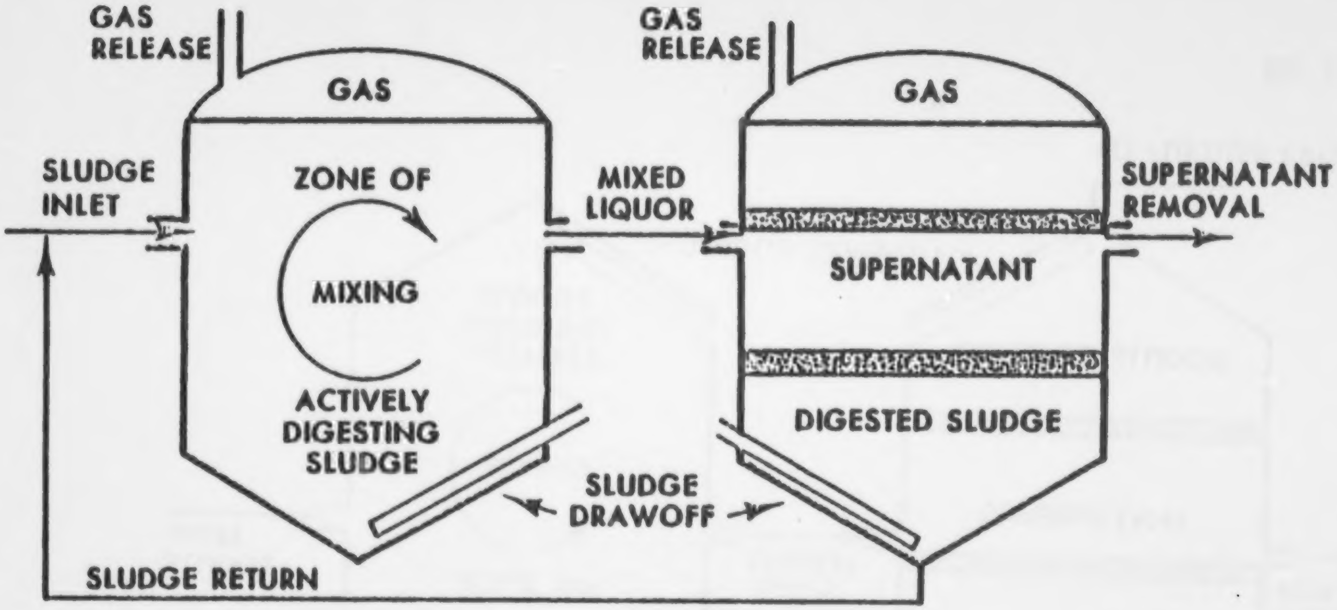
EN-325

FIGURE 1. STANDARD RATE AND HIGH RATE DIGESTION


GAS
RELEASE
GAS
SLUDGE
INLET
ZONE OF
MIXING
ACTIVELY
DIGESTING
SLUDGE
MIXED
LIQUOR
GAS
RELEASE
GAS
SUPERNATANT
REMOVAL
SUPERNATANT
DIGESTED SLUDGE
SLUDGE DRAWOFF
TO FURTHER PROCESSING

EN-325

FIGURE 2. TWO-STAGE ANEROBIC DIGESTION


GAS RELEASE
GAS
SLUDGE INLET
ZONE OF
MIXING
ACTIVELY DIGESTING SLUDGE
MIXED LIQUOR
GAS RELEASE
GAS
SUPERNATANT
DIGESTED SLUDGE
SUPERNATANT REMOVAL
SLUDGE DRAWOFF
SLUDGE RETURN

EN-325

FIGURE 3. ANAEROBIC CONTACT DIGESTION

Process Reliability:

Complexity - This process is complex because specific temperature and alkalinity levels need to be maintained. The analytical monitoring required for this system also adds to its complexity.

Start-up and Shutdown - Seeding of this system from a well operating sewage sludge digestor and careful addition and withdrawal of sludge required for start-up. This can be a difficult procedure.

Equipment - The basic anaerobic digestion process unit consists of a circular tank with a cover, either fixed or floating. The equipment is readily available.

Materials of Construction - No unusual materials are required for this process.

Raw Materials - None other than seed sludge.

Secondary Pollutants: The digestor supernatant is high in suspended solids, BOD, and ammonia nitrogen. This wastewater is normally recycled to the head of the treatment plant. Evolved methane gas requires proper venting or recovery.

Applicability: Anaerobic digestion has not been applied to waste biosludges from refineries. Further study is required to determine its applicability.

Process Advantages:

- Methane Recovery.
- Solids stabilization and enhancement of dewatering properties.
- Small process area required.
- Volatile solids destruction.
- Use of digested sludge as fertilizer or soil conditioner.

Process Disadvantages:

- Temperature control required.
- Alkalinity control required.
- Skilled operation required.
- Excess volatile acids generation can cause process upsets.
- Odors.
- Explosion hazard.

Costs and Energy Requirements:

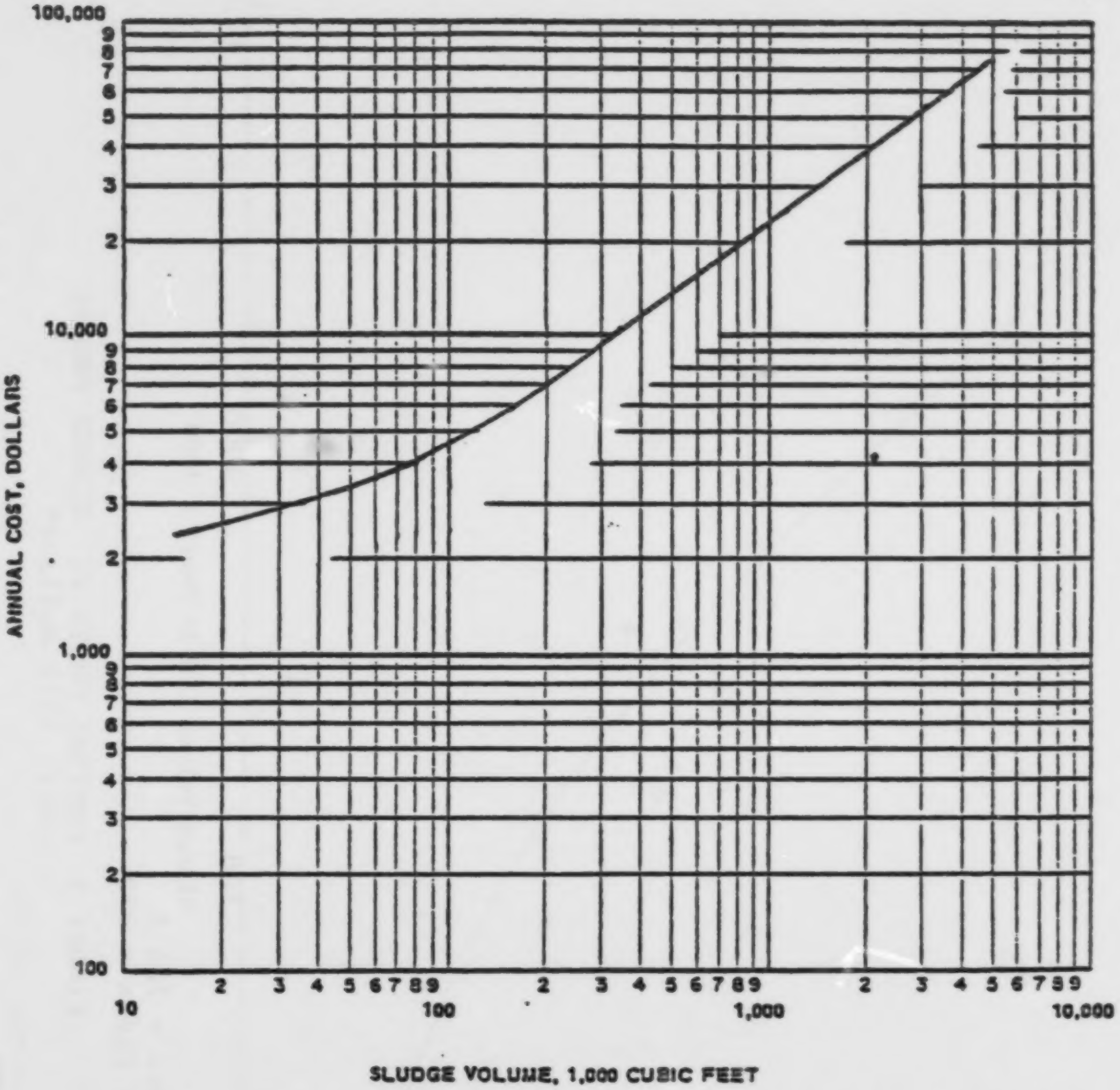
Capital Costs: Figure 5 shows the relationship of capital costs to digested sludge volume.

Operating Costs: Figure 4 shows the relationship of annual operating costs to digested sludge volume.

Energy Requirements: Energy is required for the pump and digestor heater. No specifics on these energy requirements are available.

Manufacturers or Developer: Numerous

References: BI-043, AM-062, CH-353, CU-082, CR-154, EN-325



July 1977 cost index = 204.5

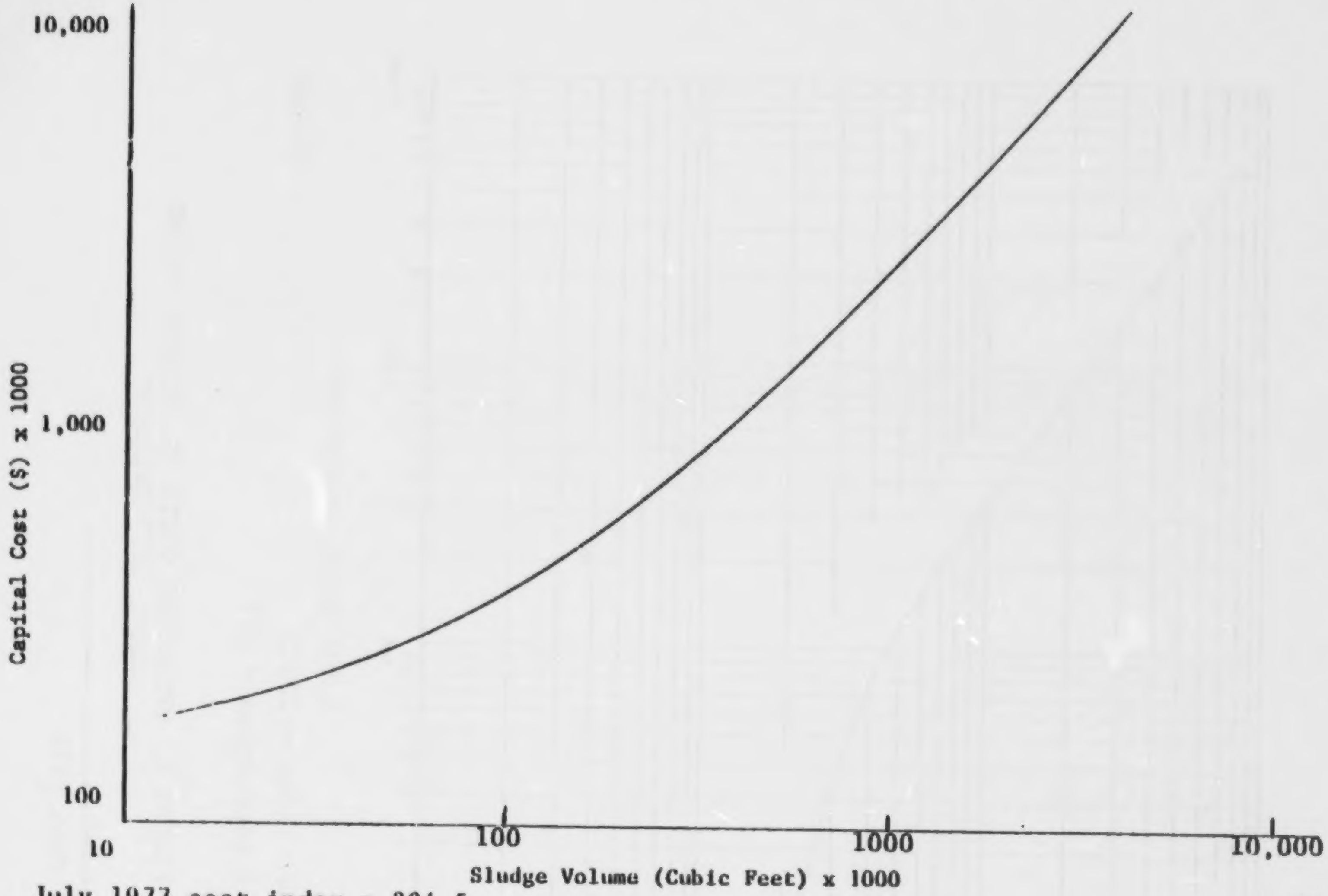
December 1978 cost index = 225

CU-082

FIGURE 4 OPERATING COSTS VS. SLUDGE VOLUME
July, 1977 Dollars*

---

*Projected from 1976.



July 1977 cost index = 204.5
December 1978 cost index = 225

CU-082

FIGURE 5 CAPITAL COSTS VS. SLUDGE VOLUME
JULY, 1977 dollars*

---

*Projected from 1976.

Process/Equipment: Chemical Fixation-Chemfix®

Application: Stabilization of Hazardous Sludges

Process Description: In the Chemfix® process, sludge is pumped into a mobile van 40 feet long and 8 feet wide. This unit contains the chemical storage, metering and mixing equipment for operating the process at flow rates of 300-500 gallons per minute. The process is continuous and occurs at ambient temperatures and pressure. Process control is maintained by automatic equipment which meters the required ratios of sodium silicate and Portland cement into the water as it flows through the van. The treated sludge then requires 24-72 hours set-up time under normal conditions before it can be excavated and trucked to landfill. The Chemfix® process chemistry consists of three reactions: first, the diffusion-controlled precipitation of nearly all heavy polyvalent metal ions with silicate ions supplied from soluble sodium silicate; second, a gel-forming reaction between the setting agent (Portland cement) and the silicate which absorbs large quantities of both water and oily solids through physical and chemical fixation; and finally, reaction of the cement with the waste and/or water further increasing the solids content. The process is not designed to reduce the permeability of the waste, but to bind the constituents together chemically. This process supplies adequate leachate quality while providing structurally stable properties. The volume of chemicals added to the waste is less than 10 percent.

Development Status: The Chemfix® process has been tested by a broad range of industries such as refineries, chemical companies, electronic companies, municipalities with sewage and landfill problems, steel plants, automobile assembly plant, power plants and others. Chemfix® has also participated in the EPA scrubber sludge disposal program underway at TVA's Shawnee plant. In this pilot plant demonstration, Chemfix® treated the clarifier underflow stream from a limestone-based turbulent contact abosrber. The clarifier and underflow averaged 38 wt percent which contained 38 wt percent fly ash on a dry basis during the filling period December 7-8, 1974. At least one Texas refinery has used this process to treat API separator bottoms and crude tank bottoms. By 1974, 20 million gallons of refinery wastes had been treated by this process.

The current status of this technology is not clear. The patent rights have recently been sold to National Environmental Controls, Inc., Metair, Los Angeles, and their marketing plans have not been defined.

Performance:

Control Effectiveness: Sludge with solid concentrations from 35-53 percent by weight have been stabilized successfully. The Chemfix® product has unconfined compressive strengths ranging from 24 to 154 psi, bulk density 1.4 g/cm^3, and permeability ranging from 5x10^{-6} to 5x10^{-6} cm/sec. (Materials with coefficients of 10^{-6} cm/sec and lower are considered impervious for civil engineering purposes.)

Process Reliability:

Complexity - Process control is maintained automatically and is relatively simple.

Start-up and Shutdown - Can be performed easily.

Equipment - Chemfix® mobile van which contains the chemical storage, metering and mixing equipment.

Material for Construction - No unusual materials.

Raw Materials - Sodium silicate and Portland cement are required for Chemfix® process. Lime addition may be needed if pH of the sludge is below 4.

Secondary Pollutants: Potential of contaminating groundwater and surface water by the leachate of Chemfixed product still exists.

Applicability: This process is used at some refineries. It has been proposed as a method of permanent stabilization of hazardous waste of old refinery lagoons and pits. It may also be a viable technique for stabilizing hazardous tetraethyl lead wastes. Further research is needed to study the applicability.

Process Advantages:

- Improve leachate quality.
- High continuous throughput rate.
- Small volume increase due to chemical additives.
- Ability to react with complex waste mixtures.
- Non-toxicity of the solid material.

Process/Equipment: Chemical Fixation-Chemfix® Application: Stabilization of Hazardous Sludges

Process Description: In the Chemfix® process, sludge is pumped into a mobile van 40 feet long and 8 feet wide. This unit contains the chemical storage, metering and mixing equipment for operating the process at flow rates of 300-500 gallons per minute. The process is continuous and occurs at ambient temperatures and pressure. Process control is maintained by automatic equipment which meters the required ratios of sodium silicate and Portland cement into the water as it flows through the van. The treated sludge then requires 24-72 hours set-up time under normal conditions before it can be excavated and trucked to landfill. The Chemfix® process chemistry consists of three reactions: first, the diffusion-controlled precipitation of nearly all heavy polyvalent metal ions with silicate ions supplied from soluble sodium silicate; second, a gel-forming reaction between the setting agent (Portland cement) and the silicate which absorbs large quantities of both water and oily solids through physical and chemical fixation; and finally, reaction of the cement with the waste and/or water further increasing the solids content. The process is not designed to reduce the permeability of the waste, but to bind the constituents together chemically. This process supplies adequate leachate quality while providing structurally stable properties. The volume of chemicals added to the waste is less than 10 percent.

Development Status: The Chemfix® process has been tested by a broad range of industries such as refineries, chemical companies, electronic companies, municipalities with sewage and landfill problems, steel plants, automobile assembly plant, power plants and others. Chemfix® has also participated in the EPA scrubber sludge disposal program underway at TVA's Shawnee plant. In this pilot plant demonstration, Chemfix® treated the clarifier underflow stream from a limestone-based turbulent contact abosrber. The clarifier and underflow averaged 38 wt percent which contained 38 wt percent fly ash on a dry basis during the filling period December 7-8, 1974. At least one Texas refinery has used this process to treat API separator bottoms and crude tank bottoms. By 1974, 20 million gallons of refinery wastes had been treated by this process.

The current status of this technology is not clear. The patent rights have recently been sold to National Environmental Controls, Inc., Metair, Los Angeles, and their marketing plans have not been defined.

Performance:

Control Effectiveness: Sludge with solid concentrations from 35-53 percent by weight have been stabilized successfully. The Chemfix® product has unconfined compressive strengths ranging from 24 to 154 psi, bulk density 1.4 g/cm^3, and permeability ranging from $5x10^{-6}$ to $5x10^{-6}$ cm/sec. (Materials with coefficients of 10^{-6} cm/sec and lower are considered impervious for civil engineering purposes.)

Process Reliability:

Complexity - Process control is maintained automatically and is relatively simple.

Start-up and Shutdown - Can be performed easily.

Equipment - Chemfix® mobile van which contains the chemical storage, metering and mixing equipment.

Material for Construction - No unusual materials.

Raw Materials - Sodium silicate and Portland cement are required for Chemfix® process. Lime addition may be needed if pH of the sludge is below 4.

Secondary Pollutants: Potential of contaminating groundwater and surface water by the leachate of Chemfixed product still exists.

Applicability: This process is used at some refineries. It has been proposed as a method of permanent stabilization of hazardous waste of old refinery lagoons and pits. It may also be a viable technique for stabilizing hazardous tetraethyl lead wastes. Further research is needed to study the applicability.

Process Advantages:

- Improve leachate quality.
- High continuous throughput rate.
- Small volume increase due to chemical additives.
- Ability to react with complex waste mixtures.
- Non-toxicity of the solid material.

Process Disadvantages:

- Limited data on leachability.
- pH adjustment.
- Undefined current status.

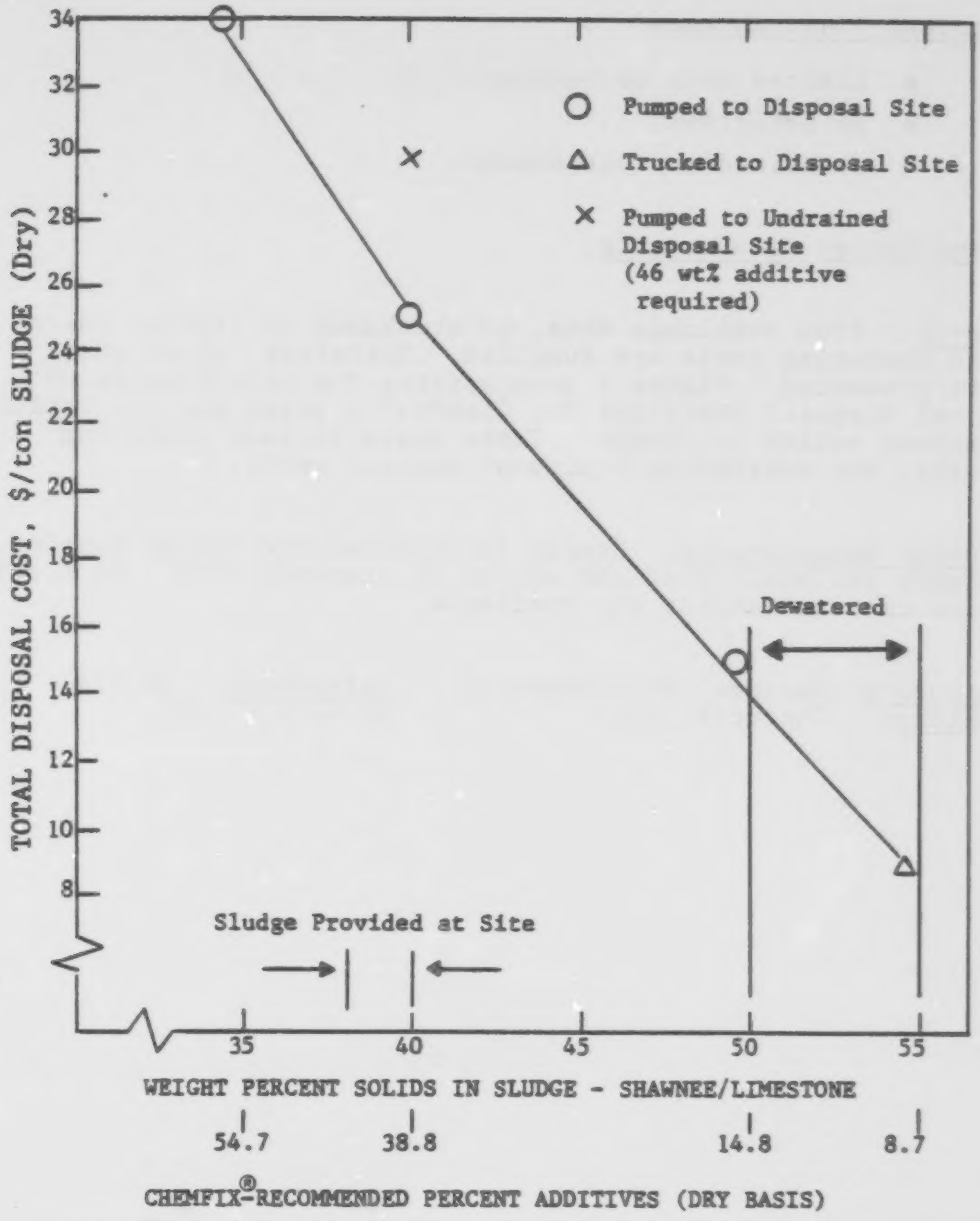
Costs and Energy Requirements:

Costs: From available data, no breakdown on capital costs and operating costs are supplied. Therefore, total costs are presented. Figure 1 demonstrates the relationship of total disposal costs for the Chemfix® process and the weight percent solids in sludge. These costs include operating costs, and dewatering equipment capital costs.

Energy Requirements: Energy is required for sludge pumping, mixing and hauling of the solids to disposal site. No specifics on requirements are available.

Manufacturers or Developer: National Environmental Controls, Inc.

References: ME-218, RO-423, WI-197



July 1977 cost index = 204.5
December 1978 cost index = 225

ME-218

FIGURE 1 AEROSPACE ESTIMATE OF TOTAL DISPOSAL COSTS FOR CHEMFIX® PROCESS. JULY 1977* DOLLARS, 1000-MW PLANT, 30-YR. PLANT LIFE, 50% AVERAGE ANNUAL LOAD FACTOR, 5 MILES TO DISPOSAL SITE

---

*Projected from 1975.

Process/Equipment: Sand Drying Beds

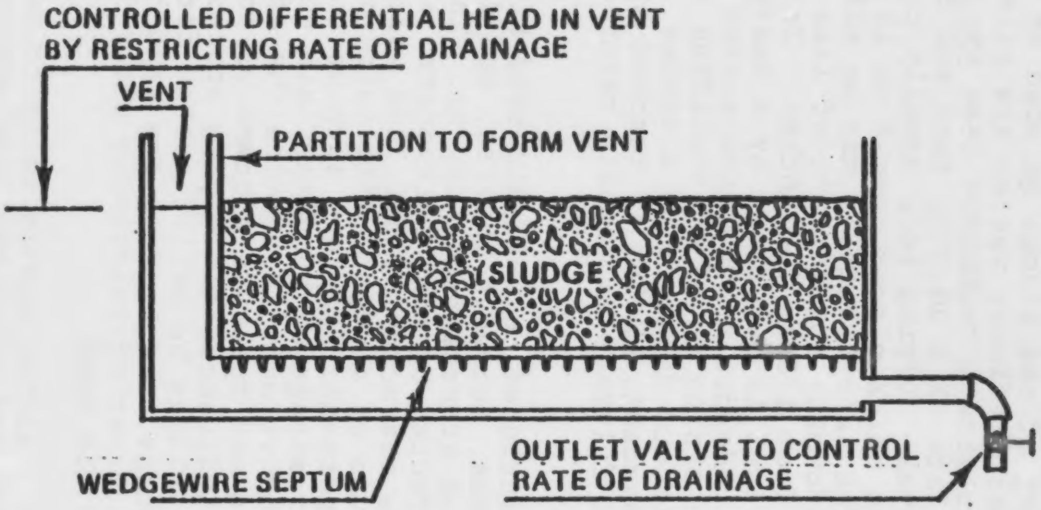
Application:
Sludge Dewatering of Low-Oil Waste Streams, e.g., Well-Digested Biosludge from Biotreatment Facilities

Process Description: The most widely used sludge dewatering method in the U.S. is drying of the sludge on open or covered sandbeds. Nevertheless, most refinery wastes are oily sludges and not amenable to this treatment technique (see Applicability below). A drying bed consists of a holding tank and filtration media made of sand and gravel. Drying beds usually consist of a layer of sand 4 to 9 inches thick placed over 8 to 18 inches of graded gravel or stone. The sand typically has an effective size of 0.3 to 1.2 mm and a uniformity coefficient of less than 5.0. Gravel is normally graded from 1/8 to 1.0 inches. In many industrial applications, the gravel is supported by a heavy wedgewire system. Drying beds have underdrains that are spaced from 8 to 20 feet apart. Underdrain piping is often vitrified clay laid with open joints, has a minimum diameter of 4 inches, and has a minimum slope of about 1 percent. Water is removed by drainage or evaporation. Collected filtrate is usually returned to the treatment plant.

Air drying is normally restricted to well-digested sludge, because raw sewage sludge is odorous, attracts insects, and does not dry satisfactorily when applied at reasonable depths. The design and use of drying beds are affected by many parameters, including weather conditions, sludge characteristics, land values and proximity of residences, and use of sludge conditioning aids. Climatic conditions are most important. Factors such as the amount and rate of precipitation, percentage of sunshine, air temperature, relative humidity, and wind velocity determine the effectiveness of air drying. The nature and moisture content of the sludge discharged to the beds also influences the drying process. It is important that wastewater sludge be well-digested for optimum drying. In well-digested sludge, entrained gases tend to float the sludge solids and leave a layer of relatively clear liquid, which can readily drain through the sand.

Dewatered sludge is removed either mechanically or manually. Figure 1 shows one type of sandbed which has been employed widely in industry. The filtration support is a heavy wire mesh often referred to as a wedgewire system.

Development Status: Over 6,000 wastewater treatment plants use this method. Although they are especially popular in small plants, drying beds are also used by 38 percent of the cities serving


CONTROLLED DIFFERENTIAL HEAD IN VENT
BY RESTRICTING RATE OF DRAINAGE
VENT
PARTITION TO FORM VENT
SLUDGE
WEDGEWIRE SEPTUM
OUTLET VALVE TO CONTROL
RATE OF DRAINAGE

EN-325

FIGURE 1. CROSS SECTION OF A WEDGEWIRE DRYING BED

populations of over 100,000. Furthermore, sandbed drying is the most common technique employed in Europe.

Performance:

Control Effectiveness: Typical performance data show rapid dewatering during the first one to two days while water removal by drainage predominates. This is followed by two to five weeks of slow dewatering principally by evaporation. In good weather, a cake of 45 percent solids may be achieved in six weeks with a well-digested sludge. As with many dewatering techniques, the performance of a bed may be improved by proper chemical conditioning and the dewatering time may be reduced by 50 percent or more.

Typical wedgewire drying bed performance data with the application of chemical conditions is shown in the following table:

TYPICAL PERFORMANCE DATA FOR WEDGEWIRE DRYING BEDS

Sludge Type	Feed Solids (Percent)	Cake Solids (Percent)	Time Interval	Solids Capture (%)
Primary	8.5	25	14 days	99
Trickling Filter Humus	2.9	8.8	20 hours	85
Digested Primary + EAS*	3.0	10.0	12 days	86
Fresh EAS*	0.7	6.2	12 hours	94
Fresh EAS*	1.1	9.9	8 days	87
Thickened EAS*	2.5	8.1	41 hours	100

*EAS = Excess Activated Sludge

EN-325

Process Reliability:

Complexity - Little operator attention and skill are required.

Start-up and Shutdown - Can be performed easily.

Equipment - Sandbeds and sludge removal equipment.

Materials of Construction - Sand and gravel, concrete, etc. No unusual material is required for construction.

Raw Materials - Sludge conditioning chemicals (e.g., flocculants and coagulants) are sometimes required.

Secondary Pollutants: Three types of secondary pollutants result from sandbed operations:

- Dewatered sludge which requires disposal.
- Odors evolved if treated sludge is not well-digested.
- Collected drainage water which is generally sent back to treatment plant.

Applicability: Some refinery sludges contain significant amounts of oil and oily solids, and are only slightly dewatered by sand filtration. The principal application of gravity filtration lies in dewatering well-digested sludge from sanitary sewage treatment, activated sludge and trickling filter solids from wastewater treatment, and solids slurries that are essentially oil-free.

Process Advantages:

- Skilled labor is not required.
- Operator attention is minimal.
- Low capital costs.

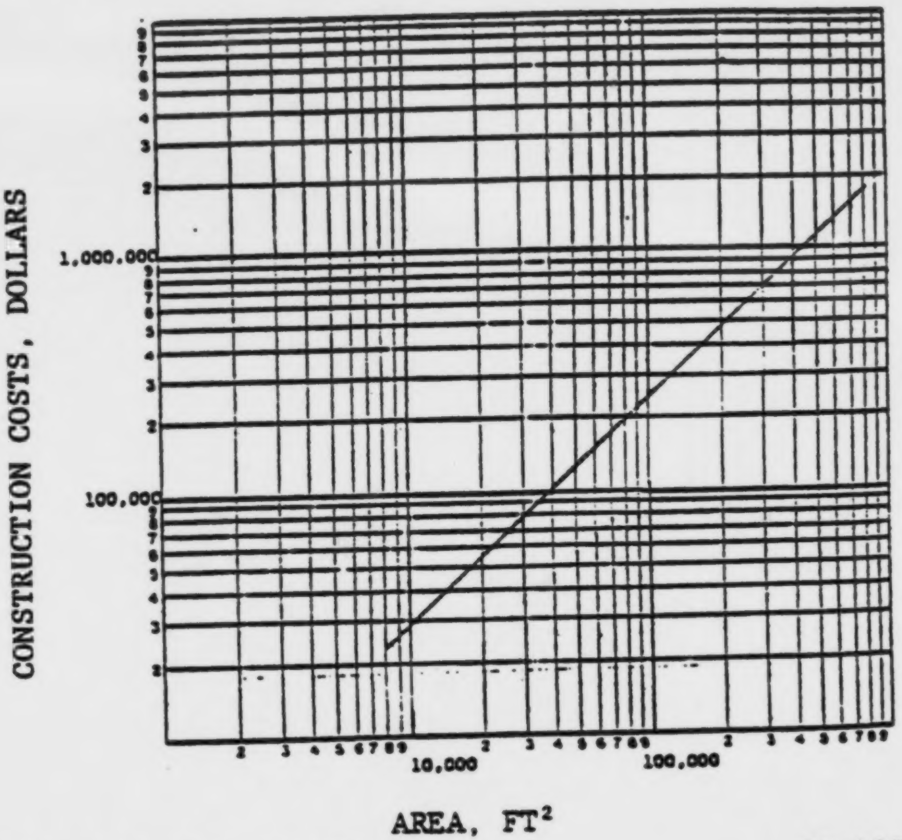
Process Disadvantages:

- Land area required.
- Weather problems for open sandbeds; e.g., freezing, odor, insects, etc.

Costs and Energy Requirements:

Capital Costs: Figure 2 shows construction costs of sand drying beds for various bed sizes. The curve includes excavation, piping for sludge distribution, sand and gravel drainage beds, and underdrain collection piping.

Operating Costs and Energy Requirements: Recent operating costs were not located; however, these costs are very small compared to other sludge dewatering methods. Energy is only required for mechanical sludge removal if employed.



July 1977 cost index = 204.5
December 1978 cost index = 225

CU-087

FIGURE 2 SAND DRYING BEDS, CONSTRUCTION COSTS, JULY 1977*

---

*Projected from 1975.

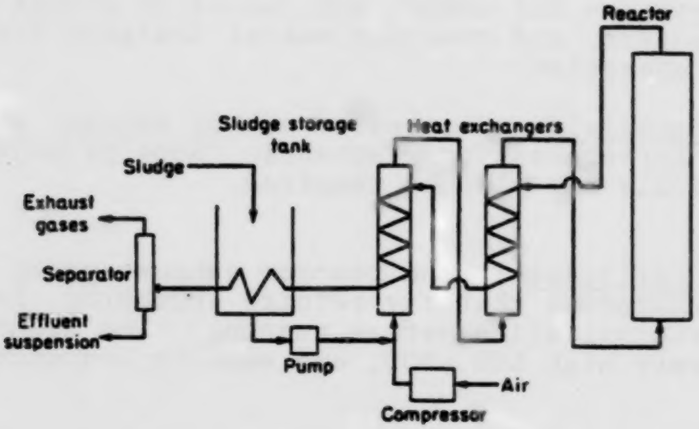
Manufacturers or Developer: Numerous.

References: AM-042, CR-154, CU-087, EN-325

Process/Equipment: Wet-Air Oxidation **Application**: Sludge Conditioning

Process Description: Wet-air oxidation, also known as wet incineration, wet combustion, or wet oxidation, is a type of thermal reduction process which is used to partially oxidize volatile organic solids present in untreated sludge and hence condition the material prior to dewatering. Wet-air oxidation occurs at elevated temperatures and pressures. A diagram of a typical flow scheme is shown below.

Sludge is preheated by exchange with the reaction products and then mixed with stoichiometric amounts of air or oxygen. The mixture enters the reactor at 350-600°F depending upon the particular application and under sufficient pressure (300 to 3000 psig) to keep the water contained in the sludge in the liquid state. The high temperature and free oxygen serve to break down the heavy organic molecules by chemical oxidation and hydrolysis. The amount of oxygen required is determined by the COD of the waste stream; excess oxygen has little effect on the rate. The oxidation process itself provides much of the necessary heat in the reactor. The process may become thermally self-sustaining for wastes in excess of 10,000 ppm COD. A mixture of gases (primarily CO_2 and N_2), water, and solids leave the reactor and are used to preheat the incoming waste before being separated in a cyclone. The liquid and stabilized solids are separated by vacuum filtration, centrifugation, or drying beds, or in dewatering lagoons. The supernatant from dewatering is recycled to the wastewater treatment plant. This high strength liquor is a major disadvantage of the process because of its substantial organic load on the biotreatment facility.



CL-039

WET-AIR OXIDATION SYSTEM

Development Status: Wet-air oxidation is a proven process developed through 30 years of municipal sludge treating and industrial applications.

Performance:

Control Effectiveness: This technique improves the dewatering properties of sludge quite dramatically. The BOD and COD content of the stabilized sludge is greatly reduced; however, these oxygen demands are concentrated in the recycle liquors. The BOD content may be as high as 40-50 percent of that of the unprocessed sludge; the COD content typically ranges from 7000 to 10,000 mg/ℓ.

Process Reliability: This process is reliable but is more complex than most treating processes. It is operated at high pressures and temperatures.

Complexity - Fairly complex. Standard concepts and equipment are used.

Start-up and Shutdown - Relatively easy.

Materials of Construction - The process employs high pressures and moderate temperatures. Corrosion resistant materials are required.

Equipment - Air compressor, water or sludge pump, heat exchangers, and reaction vessel designed for high pressure operation.

Raw Materials - Compressed air or oxygen, and steam or fuel for preheating reactants. Some pH adjustment chemicals may also be required.

Secondary Pollutants: The reactor exhaust gases may contain odorous substances that may require scrubbing, incineration, or catalytic oxidation before venting. The liquid effluent contains very high COD, BOD, and ammonia concentrations.

Applicability: One refiner reported development of a skid or truck-mounted wet-air oxidation unit; the mobility of the equipment permits emergency solid waste management during shutdown.

Costs and Energy Requirements:

Capital Costs: The costs graphically presented in Figure 1 have been updated to July 1977. The assumed operating conditions are 1500 psig and 550°F (HU-236).

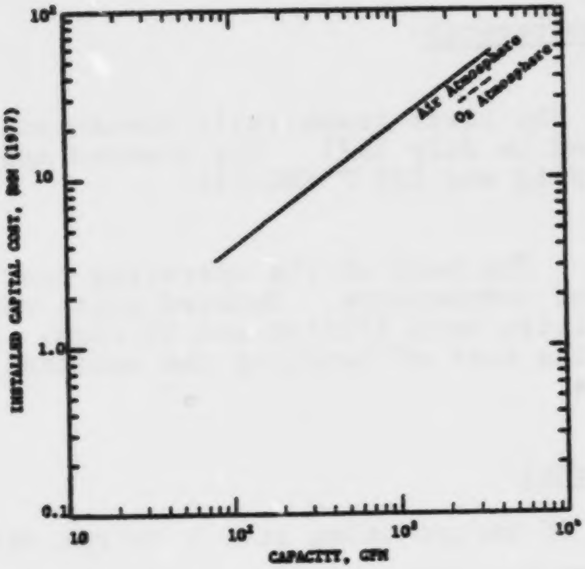
Operating Costs: The bulk of the operating cost is for power for the pumps and compressors. Updated costs reported by two municipal facilities were $27/ton and $37/ton. These values do not include the cost of handling the oxidized solids or recycled liquors.

Energy Requirements:

- Power: 25 kw/gpm using air; 5 kw/gpm using oxygen.
- Maintenance: less than 3 percent of capital costs per year.
- Some energy may be required for heating the reactor. However, for waste streams with over 10,000 ppm COD the reaction becomes thermally self-sustaining and little heat input is required.

Manufacturers or Developer: Several.

References: CL-039, EC-008, EN-325, GO-279, HU-236, ME-095, ME-294



July 1977 cost index = 204.5

December 1978 cost index = 225

FIGURE 1 APPROXIMATE CAPITAL COSTS FOR WET OXIDATION TREATMENT SYSTEMS

Process/Equipment: Composting

Application:
Waste Biological Sludges
with Oily Wastes

Process Description: Composting is the process of biochemical degradation of organic material under controlled conditions to a stable end product. Most composting operations consist of three steps:

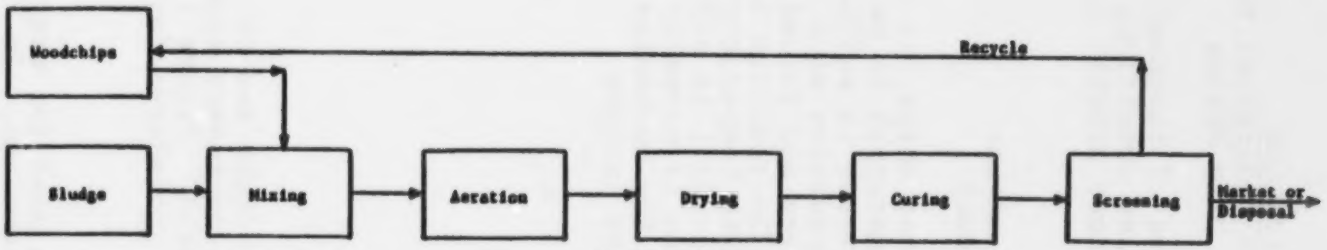
1) Preparation of the wastes
2) Decomposition/airing of the prepared wastes
3) Preparation and marketing of the product

The addition of a bulking material, such as wood chips, is required to adjust the moisture content of the material to be composted. A wet weight of 45 to 65 wt percent water is sufficient. Decomposition occurs by aerobic bacterial degradation with oxygen supplied by turning/mixing in windrow composters and forced ventilation in mechanical aeration systems. The reaction is exothermic and the wastes reach the thermophilic temperature range (140-160°F). Virtually complete pathogen kill is effected at these temperatures. The period of digestion is normally about six weeks for windrows and several days for mechanical aeration systems. Important process parameters include:

- Moisture content
- Temperature
- Oxygen transfer rate
- CO_2 emission rate
- pH
- Porosity
- C/N ratio

After sufficient digestion, measured by temperature and CO_2 emission rate, the compost is cured to insure the necessary stabilization before screening and final disposal or sale. Figure 1 illustrates a general flow diagram with operating procedures for the two major composting systems.

Development Status: This technology has been used for many decades in Europe as a refuse and sludge treatment technique. In the U.S., its use has been largely confined to municipal refuse disposal. One refinery, however, has conducted a full-scale test and reported successful results.


Woodchips
Sludge
Mixing
Aeration
Drying
Curing
Screening
Recycle
Market or Disposal

Composting System		Time in Each Stage				
1. Windrow	Bulking	Piled-½ day	32-42 days	2 days	20 days	½ day
2. Mechanical Aeration	Bulking	Placed in a Mechanically aerated pile-½ day	21 days	2 days	30 days	½ day

FIGURE 1

FLOW DIAGRAM AND TIMES REQUIRED FOR COMPOSTING IN TWO DIFFERENT SYSTEMS

Performance:

Control Effectiveness: Approximately 20 to 30 percent of the volatile solids are converted to carbon dioxide and water. The compost is free of pathogens and spores. It has been found that 20 to 50 percent less landfill space is required for composted material.

Process Reliability: Not proven as a process on refinery sludges.

Complexity: Skilled labor is required.

Start-up and Shutdown: Initial seeding and proper moisture content can make start-up difficult. Careful monitoring is required throughout.

Equipment: Composting bins for some mechanical aeration systems; blowers or agitation equipment for aeration are required as well as screening equipment.

Materials of Construction: No special materials are required.

Raw Materials: Wood chips or other bulking material; chemical conditioners are sometimes required. Initial seed compost is necessary.

Secondary Pollutants: Composted material must be disposed of in a landfill or by other final disposal methods. No odor problems are generated from properly managed composting systems. Air emissions from windrow piles has yet to be investigated.

Applicability: Preliminary testing indicates that composting could be applied to mixtures of biological solids and oily sludges. Further evaluation should be conducted to determine the flexibility of composting systems to accomodate different feed sludges.

Process Advantages:

- Possibility of year-round operation.
- No groundwater monitoring required.
- Solid waste is reduced in volume and weight and this extends the life of land disposal facilities.
- Degrades waste rather than stores it.
- Composted material is sanitary and humuslike.
- Can be used as a soil conditioner.
- Possible revenue from product.

Process Disadvantages:

- Insufficient testing on refinery sludges.
- Economics are currently unclear.
- Skilled operation and monitoring required.

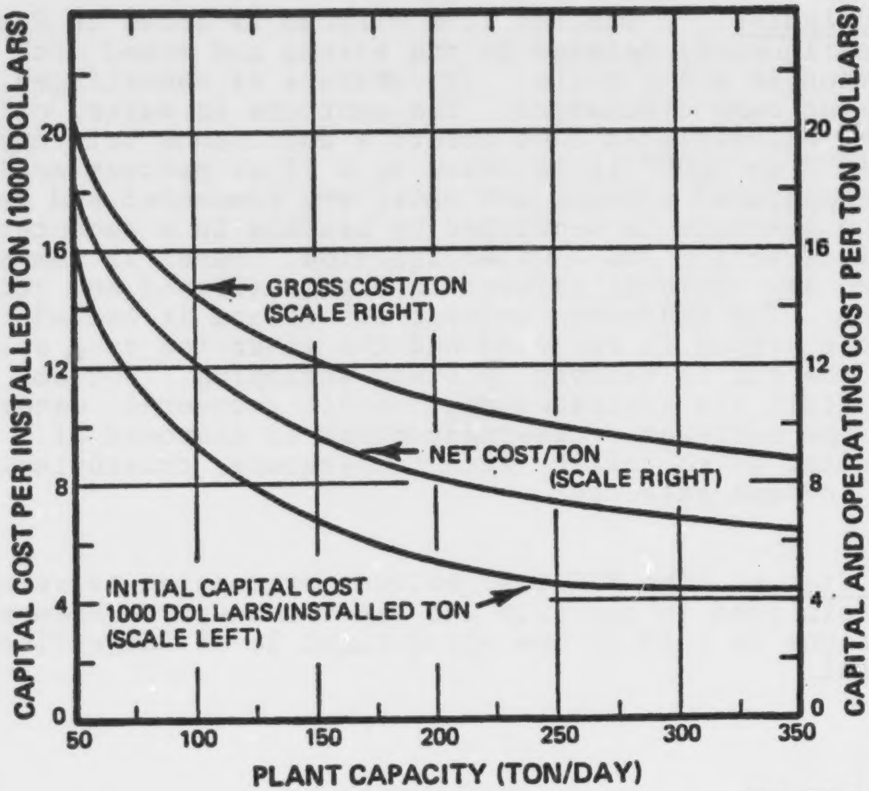
Costs and Energy Requirements:

Costs: Capital and operating costs are highly variable for composting depending on the type of waste, the type of composter, and the capacity. A range of $2 to $20/ton have been reported. Figure 2 shows some typical cost data. Revenues from the sale of composted product range from $2.00 to $4.00 per ton of material fed.

Energy Requirements: Energy is required for feed and mixing augers and the blowers for mechanical aeration units. Tractors or other turning/agitation equipment is necessary for windrow operation. No specific data are available on energy requirements.

Manufacturers or Developer: Numerous.

References: EN-325, KN-055, LI-120, ME-294



EN-325

NOTES:

1. Plant capacity is normally one or two shifts per day to achieve plant capacity.
2. Gross cost trend is the owning and operating facilities without any credits.
3. Net cost trend is for owning and operating facilities considering sales of compost and salvaged materials.
4. All costs consider compost digested sludge with refuse.
5. Source: Composting of Municipal Solid Wastes in the United States, US Environmental Protection Agency (1971).

1971 Cost Index = 132.2

Dec. 1978 Cost Index = 225.0

FIGURE 2

CAPITAL AND OPERATING COSTS FOR A COMPOSTING SYSTEM

Process/Equipment: B.E.S.T. Solvent Extraction Process Application: Sludge Dewatering

Process Description: A process flow diagram is shown in Figure 1. Sludge is continuously metered to the system and mixed with recirculated solvent in a 6:1 ratio. The mixture is centrifuged and the solvent-wet cake discharged. The centrate is water, oil, and solvent. The oil-depleted cake enters a continuous belt dryer where, at 240°F to 350°F it is dried to a 95 wt percent solids cake. The evaporated solvent and water are condensed and recirculated. The centrate is separated by heating in a decanter into a solvent/oil fraction and a water fraction. Water is pumped to a still where any residual solvent is steam stripped and returned to the system. The separated solvent/oil stream is cooled to 15°F and split; one stream is recycled and the other fed to a solvent still where the oil is removed by steam stripping. Bottoms from the solvent still are separated and the oil recovered; water is returned to the wastewater treatment plant or disposed of. Due to its variation of solubility with temperature, triethylamine is usually the solvent selected.

Development Status: The B.E.S.T. solvent extraction procedure is being commercialized in the pulp and paper industry. However, such a technique is only at the pilot plant level for refinery waste disposal.

Performance:

Control Effectiveness: Oil is recovered, and a very dry cake (95 percent solid) is discharged. Pathogen kill is complete in the dryer. Much flexibility in the feed sludge composition is permissible; the final product is very consistent. Dissolved solids are not removed in this process; they appear in the effluent from the water still.

Process Reliability:

Complexity - This is a complicated process with skilled labor or sophisticated automatic control required.

Start-up and Shutdown - This presents no particular problems.

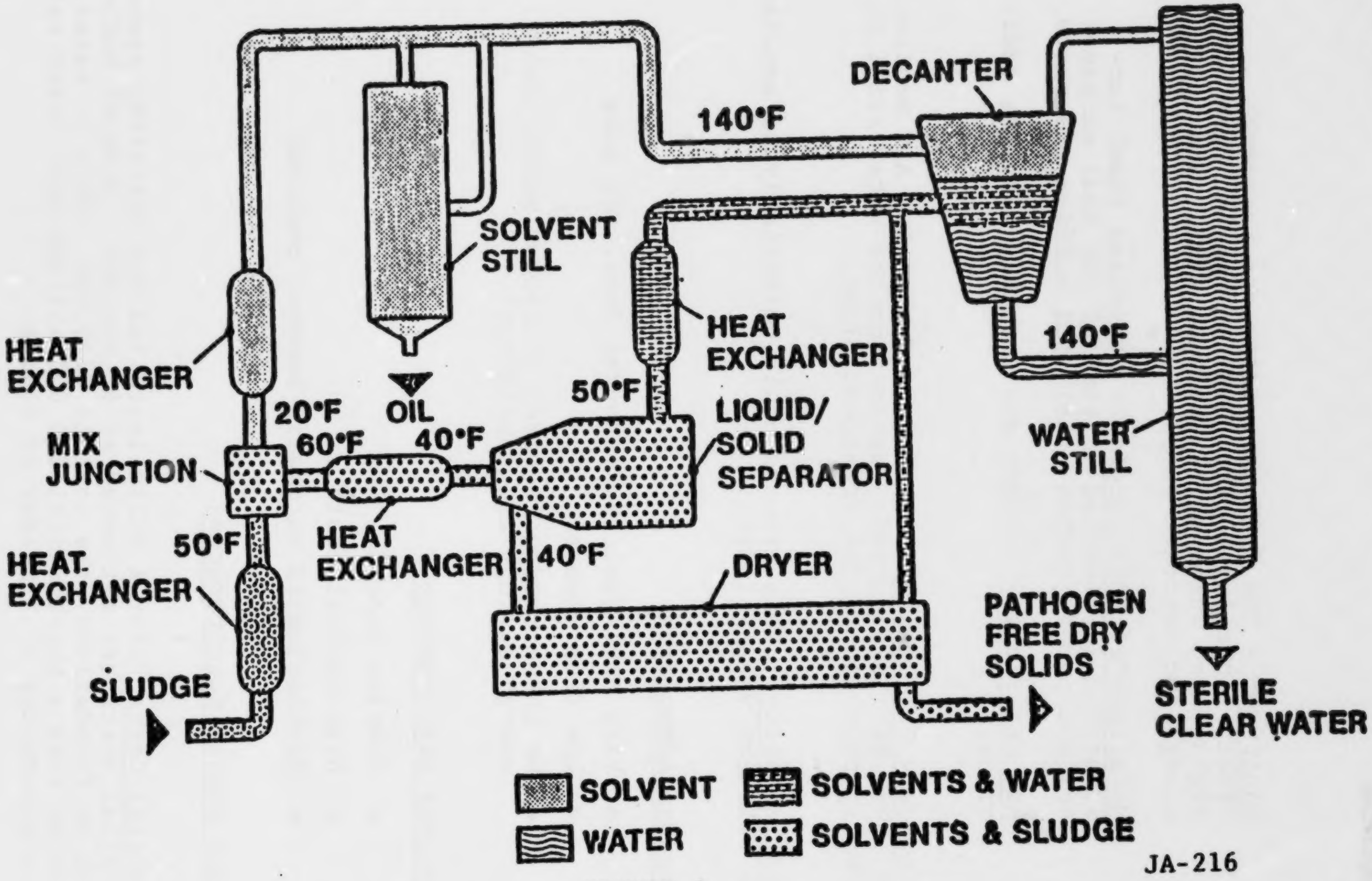

HEAT
EXCHANGER
MIX
JUNCTION
HEAT
EXCHANGER
SLUDGE
20°F
60°F
50°F
SOLVENT
STILL
OIL
40°F
HEAT
EXCHANGER
140°F
DECANTER
HEAT
EXCHANGER
50°F
LIQUID/
SOLID
SEPARATOR
40°F
DRYER
PATHOGEN
FREE DRY
SOLIDS
140°F
WATER
STILL
STERILE
CLEAR WATER
SOLVENT
WATER
SOLVENTS & WATER
SOLVENTS & SLUDGE
JA-216

FIGURE 1

FLOW DIAGRAM OF B.E.S.T. PROCESS

Equipment - The following units are required: dryer, centrifuge, refrigeration system, heat exchangers, water still, solvent still, and sludge and centrate pumps.

Materials of Construction - Stainless steel construction is mandated in some of the heat exchangers and pumps; carbon steel will suffice elsewhere.

Raw Materials - Solvent and possibly alkaline additives.

Secondary Pollutants: Cake needs disposal. Air monitoring on dryer may be required. Water from the water still is usually recycled to the treatment plant.

Applicability: This process could potentially be applied to refinery waste sludges.

Process Advantages:

- Very high quality, pathogen free, dry cake.
- Low floor space.
- No phase change required to remove water; hence, energy savings are substantial.

Process Disadvantages:

- Complex process.
- High capital costs.
- Sophisticated automatic control required.

Costs and Energy Requirements:

Capital Costs: For a fully installed and operating system, capital costs are estimated at $2,440,000. Without building or foundations, the cost is $730,000. This is based on wastes from a hypothetical 200,000 bbl/day Gulf Coast refinery generating 80 tons/day of sludge.

Operating Costs: For a hypothetical 200,000 bbl/day refinery generating 80 tons of oil/water/sludge per day, total operating costs are estimated $26/ton. This does not include amortization of the capital.

Energy Requirements:

Thermal Energy	15,500 Btu/lb solids
Electrical Energy	.40 kwh/lb solids

Manufacturers or Developer: Resources Conservation Company

References: JA-216

Process/Equipment: Landfill

Application:
Ultimate disposal, Usually of Dewatered Sludges

Process Description: A landfill currently serves as a final disposal technique for solids and sludges. Because of its lack of significant biodegradation, this classification is being called into question. A landfill site is more properly termed a storage technique. Two types are commonly encountered, sanitary landfill and secure landfill. The sanitary landfill is an engineered method of disposal which involves spreading and compacting the waste into cells, and covering it each day with earth in a manner that poses no threat to the public health or the environment. Oily wastes are attacked by soil microorganisms and partially decomposed. The main problems in a sanitary landfill are the production of leachate that may contaminate the groundwater and the accumulation of gas that may catch fire or cause explosion. A basic configuration of a sanitary landfill is shown in Figure 1A.

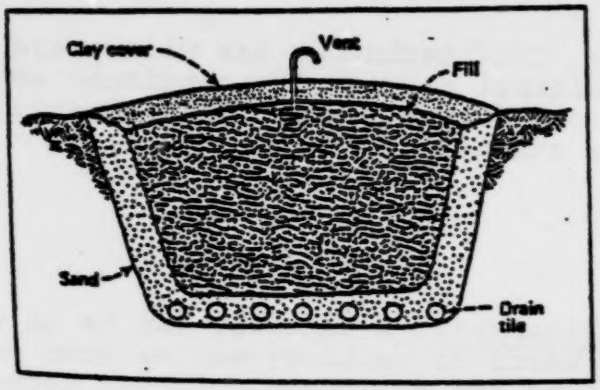
A secure landfill (used synonomously with California Class I landfill) is similar to a sanitary landfill in nature. However, a secure landfill has the following characteristics:

- Use of sealant to minimize pollution.
- Reroute of surface water at landfill site if needed.
- Water table is below the landfill site.
- Provisions of leachate collection and treatment, monitoring wells and venting, as needed.
- Segregation of incompatible wastes.

Figure 1B demonstrates one possible design for a secure landfill. Pollution potential still exists for secure landfills for a prolonged period of time.

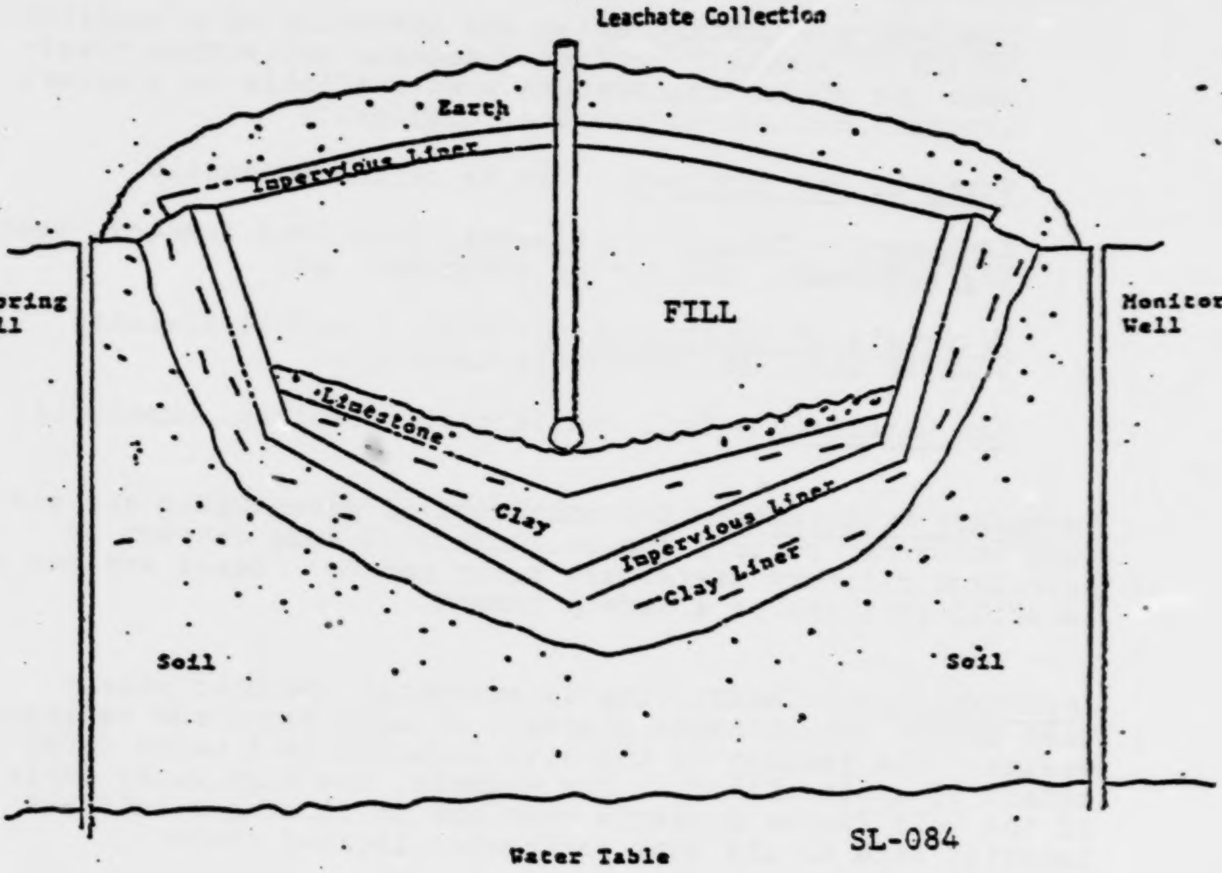
The important operating parameters for landfills are:

- Hydraulics of surface and subsurface waters.
- Soil permeability
- Site geology
- Properties of input sludges
- Leachate quality


Clay cover
Vent
Fill
Sand
Drain tile

SL-084

FIGURE 1A. GENERAL CONFIGURATION OF A SANITARY LANDFILL


Leachate Collection
Earth
Impervious Liner
FILL
Monitoring Well
Monitoring Well
Limestone
Clay
Impervious Liner
Clay Liner
Soil
Soil
Water Table

SL-084

FIGURE 1B. ONE POSSIBILITY OF A SECURE LANDFILL

Development Status: This technique has widespread use for disposal of refinery and municipal wastes. Its continued employment is highly contingent upon future regulations, especially those pertaining to leachate quality.

Performance:

Control Effectiveness: A landfill can be an effective ultimate disposal means of refinery wastes when pollution preventive practices are exercised. Choice between sanitary landfill and secure landfill depends on the properties of solid wastes. The effectiveness is also contingent upon site-specific geological and climatological conditions.

Process Reliability:

Complexity - Configuration and operation of a landfill itself is simple. However, leachate collection treatment and monitoring systems when available in a secure landfill can add operational complexity.

Start-up and Shutdown - Can be performed easily.

Equipment - Trucks, bulldozers, front-end loaders, venting equipment, monitoring equipment, etc.

Materials of Construction - Soil, landfill sealants such as clay, and synthetic materials.

Raw Materials - Soil and leachate treatment chemicals.

Secondary Pollutants: Contamination of groundwater and surface water may occur. The pollutants of some concern in petroleum refinery wastes are heavy metals. Gases evolved at landfill site can be a safety hazard.

Applicability: Landfilling is currently the most widely used method for ultimate disposal of many petroleum refinery wastes. The geology of the site location is a major determinant of applicability. For example, the high water table of the Gulf States presents problems in finding a suitable landfill site to the many refineries located there.

Process Advantages:

- Economical ultimate disposal of solids.
- Possibility of reclaiming landfill site when completed.
- Design data readily available.

Process Disadvantages:

- High degree of maintenance required especially when leachate collection, treatment, and monitoring are performed.
- Possibilities of groundwater pollution and safety hazard caused by evolved gases.
- High land requirements.

Costs and Energy Requirements:

Capital Costs: The magnitude of capital cost depends on the landfill size and the complexity of the landfill. From EPA published data, sanitary landfill costs less than $3/ton.* Table 1 summarizes the capital costs for a sanitary landfill. Capital costs for secure landfill are highly site specific. Costs depend on size, leachate collection and monitoring systems, type of sealant, etc. No generalized conclusion can be drawn for secure landfills.

Operating Costs: Operating cost depends mainly on the cost of labor and equipment maintenance, the method of preparation, and the efficiency of the operation. Operating cost reported by EPA for sanitary landfill ranges from $1.50/ton to $9 ton.**

Energy Requirements: The energy requirements are for hauling the solid material to the disposal site, which is highly site specific, and for operating the landfill equipment.

Manufacturers or Developer: Not applicable

References: LI-120, EN-605, JO-273, SL-084, WI-331, PE-224, EN-602, KN-055, VA-203

---

*Projected from 1975.

**Projected from 1976.

TABLE 1

CAPITAL COSTS FOR A SANITARY LANDFILL (Dec. 1978 Dollars)(1)

Item	Site 1 (50 TPD), $/ton
Planning and Design	0.14
Site Development	0.07
Facilities	.03(2)
Equipment	2.03
Total	2.28

EN-602

---

(1) Projected from 1975.

(2) Includes fencing.

- Soil temperature
- Local evaporation rate
- Hydraulics of surface and sub-surface waters
- Metals accumulation
- Leachate quality and quantity
- Soil nutrients
- Site grading and runoff

Low pH (below 7.0) may cause leaching of metals. Runoff must often times be collected and routed into the refinery wastewater system. If soil nutrients (nitrates and phosphates) are low, these must be added to the soil. Periodic sampling of leachate using monitor wells or core samples from the site is necessary; further, draft regulations promulgated under RCRA may require leachate collection systems in some instances. In general, heavy metals are in lower concentration in refinery sludges than in municipal sludges. Most refiners and API recommend that crops not be grown on landfarms.

Development Status: Landfarming has been used in the petroleum industry for 25 years. Because of its economic and ecological advantages, landfarming is becoming the most common method of acceptably disposing of oily wastes.

Performance:

Control Effectiveness: Landfarming is an effective sludge disposal method when pollution preventive practices are exercised. As in landfilling, site-specific conditions, primarily climatological, determine the control effectiveness. Research by API is currently being conducted on polynuclear aromatics degradation in landfarms; air emissions are also being investigated.

Process Reliability:

Complexity - Configuration and operation of land spreading are simple. However, site monitoring requires analytical capability.

Start-up and Shutdown - Can be performed easily.

Equipment - Trucks, tilling, and monitoring equipment.

Materials of Construction - None.

Raw Materials - Nutrients and pH adjustment chemicals when required.

Secondary Pollutants: Contamination of groundwater from soil seepage and surface waters from runoff may occur. Collection and treatment of runoff may be necessary. Odors may be produced when site is not properly operated.

Applicability: The use of land spreading as a final disposal technique for refinery wastes is rapidly increasing. It is suitable for disposal of almost any oily wastes generated by a refinery. An operating landfarm has processed the following sludges:

- Tank cleanings, including crude and distillate tank bottoms and slop oil emulsion tank cleanings.
- API separator bottoms.
- Desalter sludges.
- Waste biological solids.
- Filter clays (on an emergency basis).
- Oil spill clean-up debris.

Finally, landfarming has been used extensively as the final clean-up step in the renovation of oily pits.

Process Advantages:

- It is an economical and relatively foolproof method when a suitable site is available.
- Can be conducted under a wide range of soil and environmental conditions.
- Improves the physical and chemical properties of soil by increasing organic matter and nitrogen content, porosity and moisture-holding capacity.
- Oily fractions are substantially degraded; in a landfill, only minor degradation of oily materials has been found to occur.

Process Disadvantages:

- Site monitoring is required.
- Odor and residual hydrocarbon problems when not properly operated.
- Large land area required.
- Collection and treatment of runoff water may be necessary.
- Long-term trace metal accumulation.

Costs and Energy Requirements:

Costs: The total cost of land spreading is reported to be $3 to $18 per ton of waste sludge. Land costs form the largest portion of these cost figures.

Energy Requirements: Energy is required for the operation of tilling equipment, but the requirement varies widely.

Manufacturers or Developer: Not applicable.

References: WI-331, LE-381, KN-054, KN-055, VA-203, Personal Communications with Juanita Galloway of Chevron, El Segundo, CA.

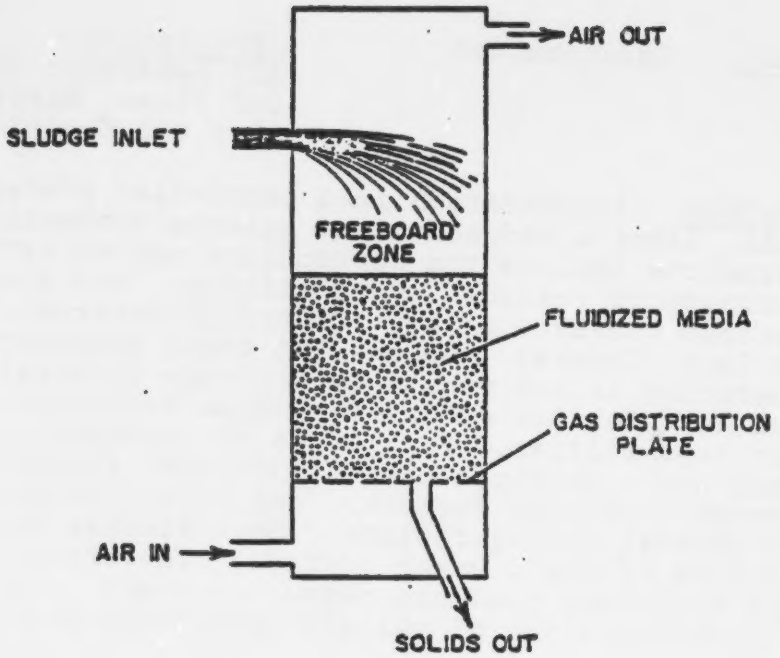
Process/Equipment: Incineration

Application:
API Separator Bottoms,
DAF Float, Waste Biosludge.
Slop Oil Emulsion Solids

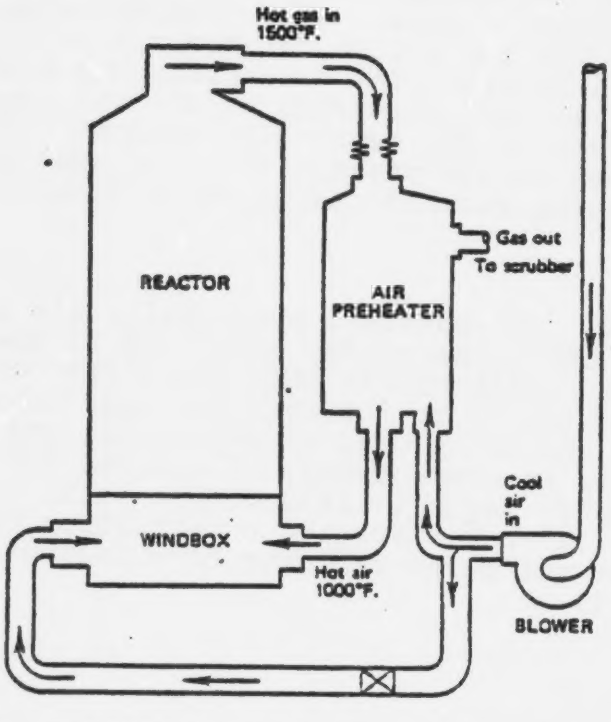
Process Description: Incineration is a controlled process for oxidizing solids, liquids and sometimes gaseous combustible wastes. Incineration products include the particulate matter carried by the gas stream, incinerator residue, grate siftings, and process water. Incinerator residue consists of noncombustible materials and requires further land disposal. Because of these secondary waste streams, incineration is not really an ultimate disposal technique but is included here for its extensive volume reduction and chemical alteration capabilities. Four types of incinerators are currently in common use: multiple hearth furnaces, fluidized bed combustion, vortex (cyclone) furnaces, and rotary kilns. Figures 1-4 show their general configurations. Most sludges will not combust easily because of their water content. Therefore, dewatering, preheating, and auxiliary fuel are needed at times. Table 1 summarizes some characteristics of the aforementioned incineration methods.

A fluidized bed, due to detention time, stable combustion temperature, and high heat efficiency, is the most promising incineration technology for refinery sludges. The heating value of the sludge must exceed 29,000 Btu per gallon to permit a self-sustaining reaction. This often necessitates dewatering the sludge to 30 percent to 40 percent solids, depending on the oil content, and supplying auxiliary fuel to the combustion chamber. Energy efficiency is aided when an air preheater is included in the configuration. Bed plugging remains the major difficulty in this technology.

Development Status: Conventional municipal-scale incinerators have been in use since 1920. As of May 1972, 193 of these plants were operating. Smaller incinerators with capacities of 5 to 12 tons per day (compared with 50 to 300 tons for most conventional municipal incinerators) are being used in commercial and industrial facilities, as well as communities. Fluidized bed incineration in the refinery industry began in 1970 with a joint AMOCO-EPA pilot unit. Successful testing warranted construction by AMOCO of a larger incinerator and other refiners have followed suit with test fluidized bed units.

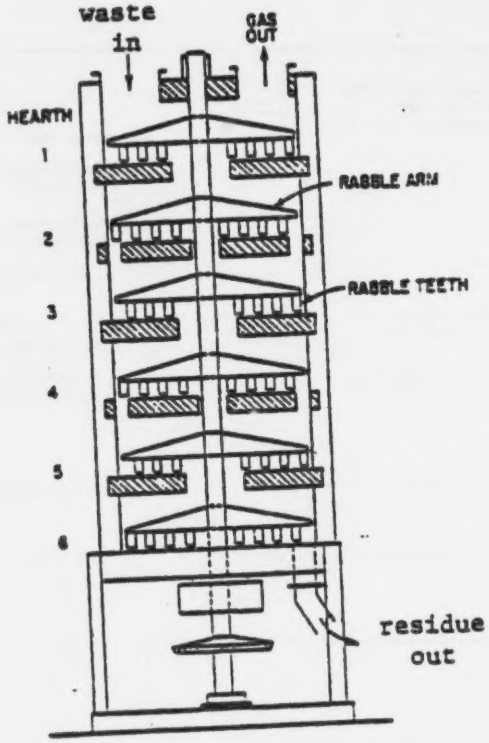

AIR OUT
SLUDGE INLET
FREEBOARD ZONE
FLUIDIZED MEDIA
GAS DISTRIBUTION PLATE
AIR IN
SOLIDS OUT
LI-120

(a) FLUIDIZED BED


Hot gas in
1500°F.
Gas out
To scrubber
REACTOR
AIR PREHEATER
Cool air in
WINDBOX
Hot air
1000°F.
BLOWER
EN-325

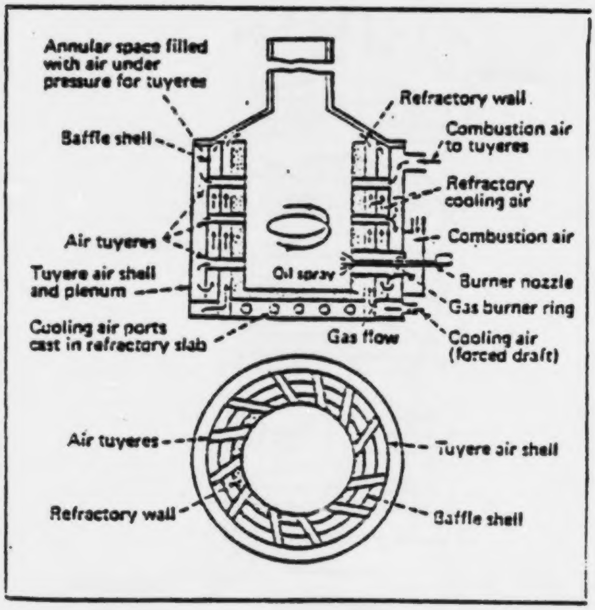
(b) FLUIDIZED BED WITH AIR PREHEATER

FIGURE 1. CONFIGURATIONS OF FLUIDIZED BED INCINERATORS


waste in
GAS OUT
HEARTH
1
2
3
4
5
6
RABBLE ARM
RABBLE TEETH
residue out

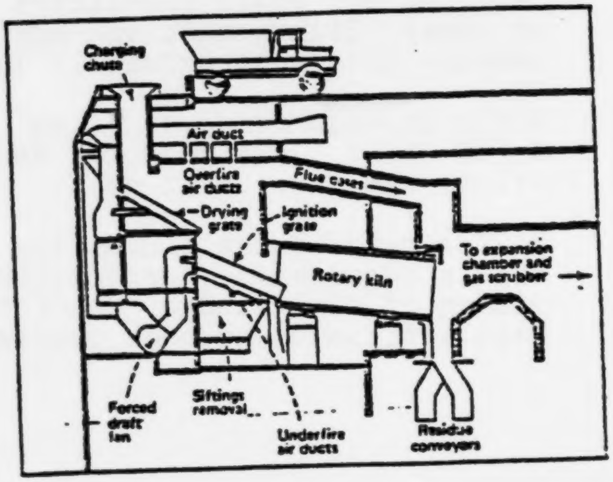
CH-196

FIGURE 2. CROSS SECTIONAL VIEW OF MULTIPLE HEARTH FURNACE


Annular space filled with air under pressure for tuyeres
Refractory wall
Baffle shell
Combustion air to tuyeres
Refractory cooling air
Air tuyeres
Combustion air
Tuyere air shell and plenum
Oil spray
Burner nozzle
Gas burner ring
Cooling air ports cast in refractory slab
Gas flow
Cooling air (forced draft)
Air tuyeres
Tuyere air shell
Refractory wall
Baffle shell

WI-331

FIGURE 3. VORTEX FURNACE


Charging chute
Air duct
Overfire air ducts
Flue gases
Drying grate
Ignition grate
Rotary kiln
To expansion chamber and gas scrubber
Forced draft fan
Siftings removal
Underfire air ducts
Residue conveyors

WI-331

FIGURE 4. ROTARY KILN

TABLE 1

CHARACTERISTICS OF VARIOUS TYPES OF INCINERATORS

Type	Characteristics
Multiple Hearth	Built in wide range of sizes, 500-2,500 lb/hr. dry solids; air cooling and auxiliary fuel are required; not very heat efficient.
Vortex (Cyclone)	Designed for small capacities (500 lb/hr. or less); lightweight and compact; low detention time (approximately 10 sec.).
Rotary Kiln	Built in wide range of sizes, 40 lb/hr. to 2,400 lb/hr.; designed for continuous operation; low investment cost.
Fluidized Bed	Silica sand is the fluidizing media, excess air is required for combustion; excellent mixing of air, sludge, and hot sand; highly heat efficient; no odor problem.

Performance:

Control Effectiveness: Incineration generally can reduce 80 to 90 percent of the total volume of solid waste, and 98 to 99 percent (by weight) of the combustible portion.

Process Reliability:

Complexity - Fairly complex, skilled labor is required.

Start-up and Shutdown - Conventional incinerators are operated continuously. Start-up requires auxiliary fuel for small industrial size incinerators. Shutdown is easy while start-up is more complicated.

Equipment - Incinerators; and pollution control equipment that could be extensive for areas (air quality control regions) with stringent air emission requirements.

Materials of Construction - Materials needed for constructing incinerator.

Raw Materials - Auxiliary fuel and sand (for fluidized bed).

Secondary Pollutants: Incineration products include the particulate matter carried by the gas stream, incinerator residue, grate siftings, and process water. Incinerator residue consists of noncombustible materials and requires further land disposal. Pollutants such as particulates, adsorbed heavy metals, NO_x, and SO_x in the exit gas may present pollution and odor problems. Mechanical collectors, and/or scrubbers may be required. After-burners on incinerator stack are commonly used to eliminate noxious odors and combustible particulates. Also, conventional incinerators may produce wastewater from wet scrubbing of off-gases which requires treatment.

Process Advantages:

- Land area required is small which is a definite advantage when land is scarce and/or expensive.
- The use of the thermal energy indigenous to oily wastes.
- Independent of geological and climatological conditions.

- Solid waste is reduced in weight and volume, and this extends the useful life of the available land disposal facilities.
- Where waste must be hauled long distances to a landfill, incineration may be economically advantageous if close-in locations can be found for the incinerator.
- Incineration is adaptable to energy recovery processes such as steam generation, and to recovery of minerals from the residue.

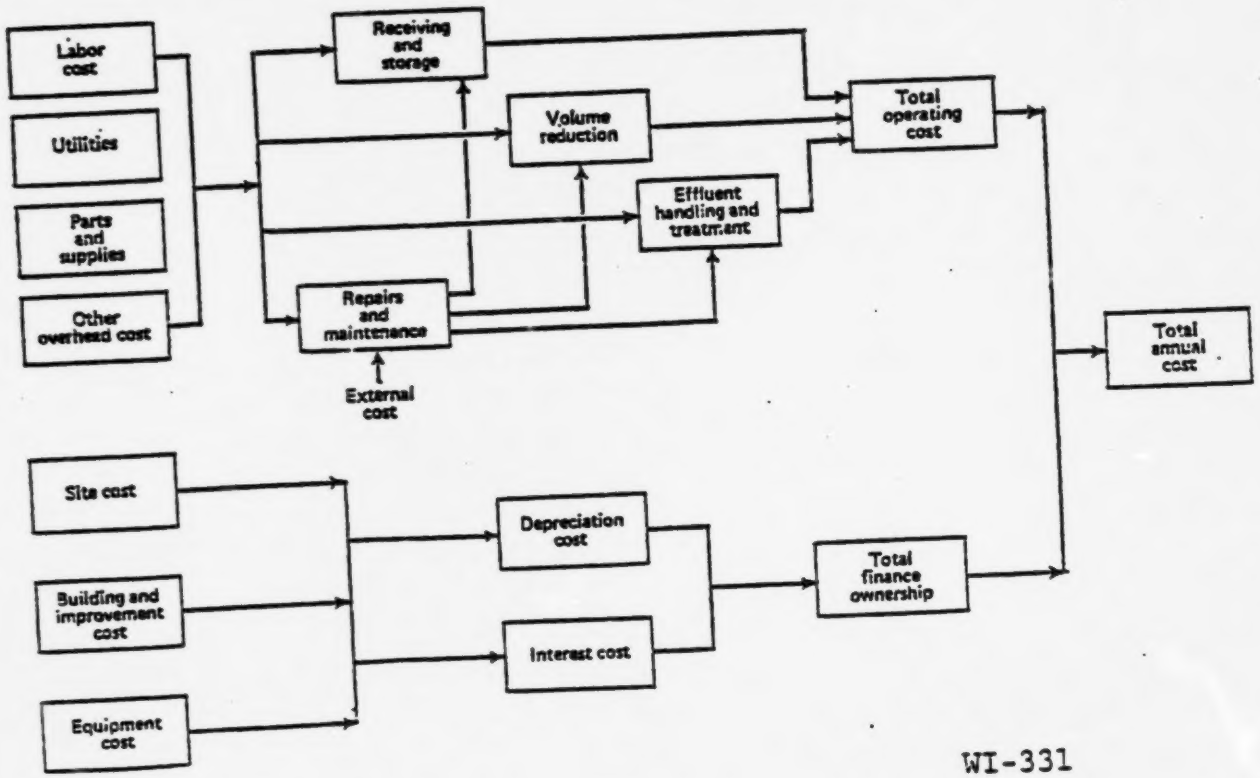
Process Disadvantages:

- Necessity for disposal of incineration residues.
- Potential for air pollutants, particularly heavy metals.
- Uneconomical for streams where much of the oil has been recovered.
- The process requires large capital expenditures and high operating costs.
- Skilled labor is required to properly operate and maintain the facility.

Costs and Energy Requirements:

Costs: Published costs have wide variations due to the different types, capacities, waste treatment facilities, sludge dewatering, etc. Figure 5 shows the allocation of incineration costs. Table 2 summarizes some of the available published costs.

Energy Requirements: Auxiliary fuel is needed for start-up maintenance, afterburner, and sometimes during incinerations. Two factors affect the amount of auxiliary fuel required for incineration: the heat value of the sludge, and the temperature required for complete combustion.


Labor cost
Utilities
Parts and supplies
Other overhead cost
Receiving and storage
Volume reduction
Effluent handling and treatment
Repairs and maintenance
External cost
Total operating cost
Total annual cost
Site cost
Building and improvement cost
Equipment cost
Depreciation cost
Interest cost
Total finance ownership

WI-331

FIGURE 5

ALLOCATION OF COSTS FOR THE INCINERATION OF SOLID WASTES

Manufacturers or Developer: Numerous

References: FE-055, LI-120, CU-082, WI-331, EN-602, CH-447, PE-224, CH-196, AM-042, RO-423, YA-089, EN-325

TABLE 2

SUMMARY OF COSTS OF INCINERATORS

Type of Incinerator	Capital Cost (Dec 1978 Dollars)	Operating Cost (Dec 1978 Dollars)	Cost Basis
Multiple Hearth	$8-$16/Ton	$7-$11/Ton	25-year payment; 500-2500 lb/hr. capacity; cost scaled up from 1973.
Vortex	$193,000	NA	200 lb/hr. capacity; size 4' x 6' x 6'; excluding dewatering; costs scaled up from 1973.
Rotary Kiln	$800-$1700/lb/hr.	NA	40-2400 lb/hr. capacity; cost scaled up from 1973.
Fluidized-bed	$390,000	$30-$45/ton dry solids	500 lb/hr capacity; capital costs include centrifuge and incineration, capital cost scaled up from 1968, operating cost from 1973.
Conventional Incinerators	$5.6 million	$10-$18/Ton	EPA data; 250 ton/day capacity; 20 year life; 6% interest; capital cost scaled up from 1971; operating cost scaled up from 1976.

NA = Not Available.

Process/Equipment: Disposal Lagoons Application: Ultimate Disposal

Process Description: This process description is similar to the description of dewatering lagoons given in the treatment subsection of this report. The major difference is that solids deposited in this type of lagoon are never removed. Typically, little if any environmental control is provided. Before government regulation spurred refiners to action, disposal lagoons were the solid waste management practice.

Disposal lagoons can only loosely be termed a control technology. Some evaporation does occur; this includes volatile organics and other compounds. Use of a pond liner would inhibit the leaching rate, however, these are seldom used. Lagoons usually consist of an excavated hole and sometimes are diked and/or dammed.

Development Status: These lagoons have been used for many years in the petroleum refining industry.

Performance:

Control Effectiveness: The major limitation to the control effectiveness of a disposal lagoon is the inability to contain either leachate or air emissions.

Process Reliability:

Complexity - A very simple process.

Start-up and Shutdown - Simple.

Equipment - No special process equipment is required.

Materials of Construction - No materials are required.

Raw Materials - No raw materials are required.

Secondary Pollutants: These ponds are seldom designed for environmental compatibility. Air emissions, coupled with a history of ineffective leachate control, have elicited heavy regulation from the government and now virtually prohibit these ponds as a final disposal technique.

Applicability: The previously mentioned regulations will eventually eliminate lagoons as a disposal technique.

Costs and Energy Requirements:

Costs: These costs are similar to those of a dewatering lagoon, given in the treatment subsection of this report. Capital and operating costs are extremely low in comparison with more environmentally acceptable technologies.

Energy Requirements: The major energy requirement for disposal lagoons is for pumping wastewater to the lagoon. The energy requirement for pumping 1000 gallons a distance of 1000 feet is about 0.5 kwhr (based upon a 5 ft/sec flow velocity).

Manufacturers or Developer: Numerous.

References: AM-042, CO-698, EN-818, RO-423

Process: Disposal Wells

Application:
Ultimate Disposal, Usually of Noxious Wastes

Process Description: Deep well disposal involves injecting refinery wastes into permeable underground formations. After suitable formations are located (typically from geological data for the area) a well is drilled and perforated into the desired formation. Wastes are pumped or injected into the well. Sufficient pressure is produced either by pumps or by the weight of the water column above the injection zone. Two major design parameters are the location and the depth selection. Because of the possible contamination of potable aquifers, many areas are not suitable for this method of disposal. In addition, seismically active areas are not suitable for deep well injection due to strains forced on the unstable formations by pressurizations of the injection zone. One operation conducted by a refinery injected wastes into three disposal wells discharging into unusable saline subterranean formations between 2100 and 4000 feet in depth.

Development Status: The technique was first developed in the oil and gas extraction industry. Few refineries currently use this methodology. Approximately 100 industrial waste injection wells presently operate in the United States.

Performance:

Control Effectiveness: Not applicable.

Process Reliability: Disposal wells have been demonstrated to be reliable for disposal of several wastewaters and oily wastes.

Complexity - Simple.

Start-up and Shutdown - Easy.

Equipment - Pumps and wastewater storage facilities above ground. Casing for well to protect shallow aquifers.

Materials of Construction - Not applicable.

Raw Materials - None.

Secondary Pollutants: The pollutants in the wastes may pollute water in nearby aquifers.

Applicability: Can be used for petroleum refinery noxious wastes depending on Federal state and local regulations. Its current application is minimal.

Costs and Energy Requirements: All of the cost and energy requirements associated with deep well disposal are highly site specific. They will depend on the availability of land with the correct geological make-up and the distance from the source of the wastes to the well. The cost of the well depends on whether an abandoned well is available. If a well has to be drilled, the cost is proportional to the depth of the well, within limits, but costs escalate very rapidly for depths of more than a few hundred feet.

Manufacturer or Developer: Numerous.

References: LI-120, EN-605, RO-423, MC-377

Process/Equipment: Ocean Disposal Application: Ultimate Disposal

Process Description: It was reported in 1974 that 600,000 tons of refinery wastes were being dumped at 120 ocean disposal sites. This method is declining as required permits become more difficult to obtain. The Marine Protection Act of 1972 (PL 92-532) transferred regulatory control to EPA. Ocean disposal of certain hazardous wastes is prohibited, and the list is growing.

Barges load sludges and other wastes in their holds and travel to a selected site before dumping the waste. The site selection is determined by distance from land, ocean currents, marine life, and ocean depth. Another method is to sequester waste in 55-gallon drums before disposal.

The principal advantage of ocean disposal is its very low cost (about $2/ton). Its inherent disadvantages are much more numerous. These include the effect on marine life, the concentration of wastes at any one disposal site, slow breakdown, and formation of surface oil slicks. Solids blanket the ocean floor and disrupt or halt the natural benthic life, with drastic effects on marine ecology. Although ocean disposal will continue for some time to come, present trends indicate it will gradually be eliminated.

Performance:

Secondary Pollutants: Hazardous wastes or solids can drastically alter marine habitats as indicated above.

Applicability: This technique is feasible only for coastal refineries.

Costs and Energy Requirements:

Costs: For large dumping, $2/ton is the approximate current cost. Containerized disposal costs range from $15 to $50/ton.

Energy Requirements: Energy is required for barge fuel.

Manufacturers or Developer: Not applicable.

References: RO-423, WI-197

APPENDIX II

DESCRIPTION OF REFINERY SOLID WASTE STREAMS

Following are descriptions of individual solid waste streams. For the purposes of this study, a "solid waste" is defined as any "refinery waste materials other than trash, garbage, and materials regulated by air emission and wastewater discharge regulations" (EN-818). The streams described were shown by the OAQPS, API and Jacobs studies to contribute significant volumes to the total solid waste load generated by the refining industry.

Slop Oil Emulsion Solids

Oils skimmed from the API separators and DAF units are usually pumped to an oil recovery tank where the mixture is separated into three phases: oil, water and emulsions. The oil is blended for reprocessing and the water is recycled to the API separator. The emulsion layer must be disposed of as a solid, or it may be further treated to break the emulsion.

Storm Water Silt

Silt which collects in the stormwater settling basins in some refineries is periodically removed, dewatered, and disposed. The quantity of silt is usually a function of the amount of rainfall and of refinery paved area, rather than of process complexity.

Exchanger Bundle Cleaning Sludge

Heat exchanger bundles are periodically cleaned during plant shutdown. Scale and sediment removed with cleaning solutions or by high pressure water are collected in sumps. The sludge is then flushed to special sumps or process sewers, shoveled, or vacuumed out and disposed of.

API Separator Sludge

Solids settle in the API separator during primary wastewater treatment for removal of free oils. These sludges are periodically removed using manual labor and vacuum trucks. API separators serve as a collection point for the oily water sewers. The bottoms, therefore, contain a mixture of all sewered wastes such as storage tank draws, de-salter wastes, laboratory wastes, sample line purges along with miscellaneous chemical leaks and spills.

Leaded or Nonleaded Product and Intermediate Tank Bottoms

Solids also settle to the bottom of distillate and residual storage tanks. The characteristics of these deposited sludges will vary according to the product stored in the tank. These tanks are cleaned when there is a change in service, product specifications cannot be met, or repairs are required.

Factors known to impact the volume and composition of the various tank sludges include:

- Crude type
- Distillate cut
- Type and quantity of chemical additives (e.g., lead)
- Recovered oil processing methods
- Use of tank mixers
- Process unit and tank metallurgy
- Product cut treatment employed upstream of tank
- Processes used in producing gasoline blend components and other distillate products

Crude Tank Bottoms

Solids in crude oil accumulate at the bottom of the crude oil storage tanks. These tanks are cleaned periodically to remove the sediment. The cleaning frequency is a function of the amount of sediment in the crude oil sent to distillation units and the reduction in storage capacity. Contaminants in crude oil tank sludges vary with the characteristics of the crude oil and the shipping and handling methods used prior to receipt at the refinery. The waste sludges, in general, consist of a mixture of iron, rust, clay, sand, water, sediment, oil, and wax.

Dissolved Air Flotation (DAF) Float

Following treatment in an API separator, the remaining oil and solids in the wastewater are removed by DAF units in many refineries. The process takes place in a vessel where the finely divided solids and oil particles are brought to the surface and skimmed off for disposal. The release of air dissolved in the wastewater causes the solid and oil particles to rise.

Kerosene Filter Clays and Other Filter Clays

Treatment with fixed bed clay is used to remove color bodies, chemical treatment residues and traces of moisture from product streams such as gasoline, kerosene, jet fuel, and light fuel oils. Clay is also used to treat lube oils by mixing the clay with the oil and subsequently removing it by filtration.

HF Alkylation Sludges

Alkylation sludges are produced by both the sulfuric acid and the hydrofluoric acid alkylation process. In most refineries spent acid from these processes will accumulate in a storage tank where sludge will settle. These sludges, containing polymerized hydrocarbons, tank scale and sulfuric acid, are removed when the tank is cleaned or repaired. The acid sludge is usually neutralized prior to disposal.

Waste Bio-Sludge

In the process of biological treatment of refinery aqueous waste streams, excess bio-sludge is created which must be wasted. The waste bio-sludge has a very high water content (80 to 99 percent); therefore, it is dewatered prior to disposal. The waste generation rate is dependent upon the type of biological treatment process, operating conditions, desired level of removal, and the raw waste load.

Once-Through Cooling Water Sludge

In the past, large volumes of water were pumped from readily available sources and passed through primary settling sumps or tanks prior to usage for once-through cooling. In refineries where once-through water is still used, silt must periodically be removed from the settling vessel.

Fluid Catalytic Cracker Catalyst Fines

Fluid catalytic cracker (FCC) catalyst is continuously regenerated by burning off the coke formed on the catalyst during the cracking process. The flue gas from the regenerator passes through a series of cyclones that recover most of the catalyst. This recovered catalyst is then returned to the reactor vessel. Because of current and future air pollution regulations, more refineries have installed electrostatic precipitators or an equivalent device to remove any catalyst fines which would otherwise be released to the atmosphere with the regenerator flue gas. These catalyst fines are disposed or in some cases sold. They are generated on a continuous basis, but are generally disposed intermittently.

Coke Fines

Coke which is produced in the course of various refinery operations, such as fluid coking and delayed coking, is sold as solid industrial fuel. Coke fines are generated intermittently, and their quantity is a function of handling techniques. A certain amount of spillage and consequent contamination with dirt results in the course of loading operations onto trucks and railroad cars. The contaminated coke is disposed.

APPENDIX III

ESTIMATION OF THE PARAMETERS OF THE LOGNORMAL DISTRIBUTION

Because of the high degree of skewness in the distribution of generation rates from refineries, conventional statistics are inadequate for efficient estimation of generation factors and their variances. In addition to the skewness, a large percentage of the refineries studied did not generate waste from all streams. These sources affect the generation factor and therefore must be considered in developing estimates for these factors.

Statistical Distribution Models for Generation Rates

A lognormal distribution was used to model the distribution of generating sources. This distribution has the property that when the original data are transformed by taking natural logarithms, the transformed data will follow a normal distribution. The lognormal distribution is often appropriate when the standard error of an individual value is proportional to the magnitude of the value. The form of the lognormal distribution is as follows:

$$f(x) = \frac{\exp\left[-\frac{(\ln x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} \qquad \text{for } 0>x>\infty$$

$$= 0 \qquad \text{for } x \leq 0$$

$$\text{Mean} = \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = \exp[2\mu + 2\sigma^2] - \exp[2\mu + \sigma^2]$$

In order to develop estimates for generation factors, the non-generating sources also had to be modeled. A mixed distribution, specifically a lognormal distribution with a discrete probability mass at zero, was used for this purpose. Letting ρ equal the fraction of nongenerating sources in the population, this distribution has the following form:

$$f(x) = \frac{(1-\rho)\ \exp\left[-\ \frac{(\ln x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} \qquad \text{for } 0<x<\infty$$

$$= \rho \qquad \text{for } x = 0$$

$$= 0 \qquad \text{for } x < 0$$

$$\text{Mean} = (1-\rho)\ \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = (1-\rho)\ [\exp(2\mu + \sigma^2)]\ [\exp(\sigma^2) - (1-\rho)]$$

Efficient estimates of the mean and variance of the population modeled by this mixed distribution have been developed [Finney (1941), Aitchison (1955)]. These estimates are as follows:

The best, unbiased estimator of the population mean generation rate is

$$GR = \left[\left(1 - \frac{r}{n}\right) \exp[(\overline{x})]\ g\left(\frac{s^2}{2}\right)\right]$$

and the best, unbiased estimator of the population variance of the emission rates is

$$v = \left[\left(1 - \frac{r}{n}\right) \exp(2\overline{x}) \left[g(2s^2) - \left(1 - \frac{r}{n-1}\right) g\left(\frac{n-r-2}{n-r-1}\ s^2\right)\right]\right]$$

where n = number of refineries

r = number of refineries not generating waste for the particular stream

$m = n-r$ = number of generating sources

$g(t)$ = infinite series

$$= 1 + \frac{(m-1)t}{m} + \frac{(m-1)^3\ t^2}{m^2 2!\ (m+1)} + \frac{(m-1)^5\ t^3}{m^3 3!\ (m+1)(m+3)} \cdots$$

$\overline{x}$ = average of the logarithm of generating sources

$$= \sum_{1}^{n-r} \ln\ (\text{generation rates})/(n-r)$$

s^2 = variance of the logarithm of generating sources

$$= \sum_{1}^{n-r} [\ln\ (\text{generating rates}) - \overline{x}]^2/(n-r-1).$$

The mean and variance formulas hold whenever there is more than one generating source (n-r>1). When only one generating source is identified, the following estimates are appropriate:

$$\text{Mean} = \frac{x_1}{n} \text{ and variance} = \frac{x_1{}^2}{n} ,$$

where x_1 is the single measured generation rate. If no generation is found (r=n), then the best estimate for both the mean and variance is zero.

Computer programs were developed during a previous study on refinery fugitive emissions for these estimators and the estimator for the mean was used for all generation factors presented in this publication. Finney (1941) showed that this estimator is more than twice as efficient as the arithmetic mean for data distributed similarly to the generation rates from the reporting refineries.

Confidence Intervals for Percent Sources Generating and for Emission Factors

Confidence intervals for the percent of generating sources were computed using the Binomial Distribution. The Binomial is used to model data when a random sample is selected and each item is classsified into one of two categories (generating or non-generating here). Exact confidence limits (level 1-α) for the estimate of percent generating can be obtained by iteration solving for P_L in

$$\sum_{i=k}^{n} \binom{n}{i} P_L{}^{i} (1-P_L)^{n-i} = \frac{\alpha}{2} \text{ for the lower limit and for } P_u \text{ in}$$

$$\sum_{i=o}^{k} \binom{n}{i} P_u{}^{i} (1-P_u)^{n-i} = \frac{\alpha}{2} \text{ for the upper limit}$$

where n = number of refineries and k = number of generating sources. Tables of these solutions, available for most cases, were used to develop 95 percent confidence intervals reported in this publication and for computing 97.5 percent confidence intervals which were used in developing confidence intervals for generation factors. 97.5 percent was selected so that 95 percent confidence intervals for generation factors would result when the estimated percent generating was combined with the estimated mean generation rate (0.975 x 0.975 = 0.95).

Patterson (1966) described how confidence intervals for the mean from a lognormal distribution can be computed using estimators developed by Finney (1941). 97.5 percent confidence intervals were computed for the average, $\bar{y}$, of the transformed data, $y = \ln$ (generation rate), using

$$C_L = \text{lower limit} = \bar{y} - 2.24 \left[s^2/(n-r)\right]^{\frac{1}{2}} \text{ and}$$
$$C_U = \text{upper limit} = \bar{y} + 2.24 \left[s^2/(n-r)\right]^{\frac{1}{2}}$$

where s^2 is the variance of the transformed data and n-r is the number of generating sources. Then, following Patterson's arguments, confidence intervals for the mean generation rate can be computed using:

$$\text{lower limit} = \exp\left[C_L\right] g(s^2/2) \qquad \text{and}$$
$$\text{upper limit} = \exp\left[C_U\right] g(s^2/2)$$

where g(t) is the series given above.

To obtain 95 percent confidence limits for the generation factors, the confidence limits for the percent generating and for the mean generation rate were combined as follows:

lower 95 percent limit for emission factor = $P_L(C_L)$

upper 95 percent limit for emission factor = $P_U(C_U)$

These confidence intervals are conservative in the sense that 95 percent is a lower bound for the confidence coefficient for the intervals.

APPENDIX IV

SELECTION OF REFINERIES FOR SUPPLEMENTARY SAMPLING PROGRAM

In order to develop a data base which is representative of refinery solid waste streams' generation rates and volatile hydrocarbon content, it is ncessary to conduct a technical/and statistically valid sampling program.

In developing a sample base for the simulation of the entire refining industry, some compromise must be made between the number of refineries sampled and the accuracy of the sample base. In March 1978, there were 285 refineries operating in the U.S. (CA-679). The U.S. refining industry could be most precisely and accurately represented by extensively sampling 285 refineries. Obtaining and analyzing such a large set of samples would be very expensive. Reducing the number of refineries sampled, reduces the costs of sampling and analyses of refinery solid waste streams, but the reduction in the number of samples also reduces the ability to accurately define the refining industry solid waste generation rates and volatile hydrocarbon content. Three sampling schemes utilized for modeling the U.S. petroleum refining industry are discussed below.

Single Representative Refinery

It is often customary to propose a "typical" or "representative" refinery model for purpose of illustration, discussion, simulation or sampling.

An example of this type of representative refinery has been defined for process analysis and stream characterization purpuses (BO-196). The flow diagram of this plant is presented in

Figure 1. The product slate for this refinery is given in Table 1, and the capacities of the various individual processing units within the refinery are shown in Table 2. This model refinery was developed under the following assumptions:

- The refinery capacity was 15,900 m^3/day (100,000 barrels/day).
- The process units shown on the flow diagram are those in common use in the refining industry.
- The capacities of the process units relative to the crude feedstock agree with the average 1974 capacities of all U.S. refineries, as shown in Table 2.
- The refinery product distribution is consistent with that of the entire refining industry in 1974, as shown in Table 1.
- The crude feedstock was a weighted composite of crudes from the major oil fields supplying petroleum to domestic refineries in 1974.

In theory, the entire U.S. refining industry could be simulated by sampling a number of these representative model refineries. Practically, however, there are a number of serious drawbacks to this simulation methods, and only a very superficial and imprecise analysis of nationwide refinery operations can be accomplished with this technique. Some of the more obvious deficiencies of this method are listed below.

- The types of refinery process units are fixed. There are, however, many refineries which utilize fewer process modules, and a number which employ more than the representative model refinery.
- The configuration of theprocess units within the representative refinery is also fixed. Although the configuration of the representative refienry can be developed, there may not be an actual refinery with these characteristics. For sampling, this approach has limited applications.

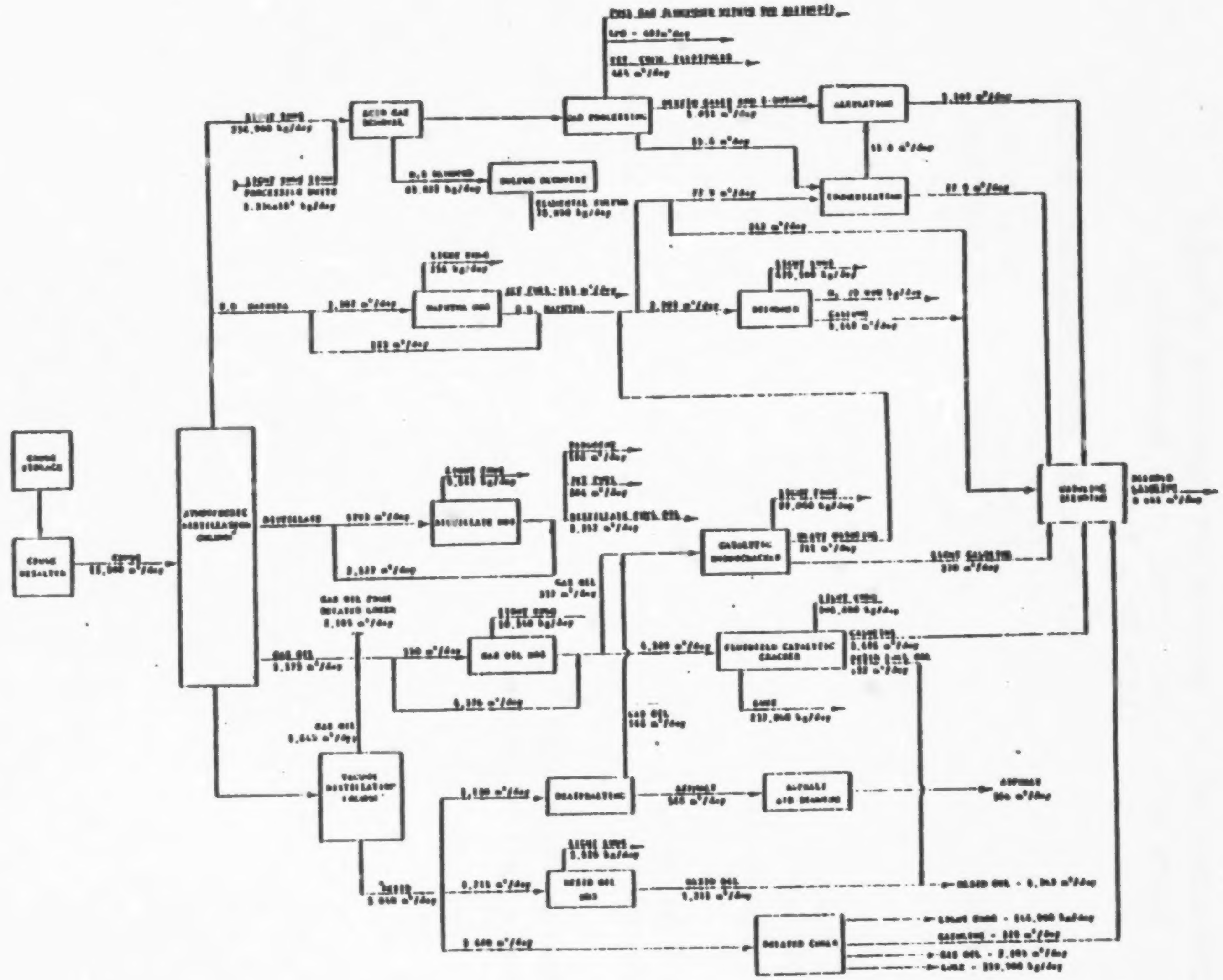


FIGURE 1. BLOCK FLOW DIAGRAM FOR A REPRESENTATIVE U.S. REFINERY

Source: BO-196

TABLE 1

COMPARISON OF "REPRESENTATIVE" REFINERY PRODUCT SLATE WITH TOTAL ACTUAL U.S. PRODUCTION
(1974 Data Base)

	Volume % of Total Refinery Products	
Product	Representative Refinery Production	Total U.S. Production
Gasoline	50.3	49.0
Kerosine	1.2	1.2
Jet Fuel,		
Naphtha Type	1.5	1.5
Kerosine Type	5.0	4.9
Distillate Fuel Oil	20.4	20.4
Asphalt	3.4	3.4
Residual Fuel Oil	8.2	8.2
Marketable Coke	1.4	1.3
LPG	2.4	2.4
Petrochemical Feedstocks	2.8	2.8
Other (Fuels, miscellaneous)	3.4	4.9
	100.0	100.0

Source: BO-196, US-209.

TABLE 2

REFINERY PROCESS UNIT CAPACITIES
"REPRESENTATIVE" COMPARED TO AVERAGE OF U.S. REFINERIES
(1974 Data Base)

Unit	Volume Percent of Crude Feedstock	
	Representative Refinery	Average of U.S. Refineries
Reformer	24.6	27.3
Fluid Cat Cracker	28.9	33.9
Hydrocracker	5.6	6.9
Coking	1.4	1.7
Asphalt	3.6	5.4
Isomerization	0.8	1.0
Alkylation	5.6	6.8
Naphtha HDS	20.8	25.2
Distillate HDS	11.3	13.7
Gas Oil HDS	3.5	4.2
Resid. Oil HDS	0.04	0.05

Source: BO-196, CA-236.

- While the representative refinery can efficiently process the selected composite crude oil, it is not suitable for refining many of the individual crudes processed by refineries across the U.S.
- The necessary specification of the individual processing units and the associated range of operating conditions further limits the utility of this model refinery for representing the entire industry.
- A model refinery may be representative of the variables considered in choosing the model refinery but may not be representative of the variables which are to be studied, e.g., solid waste generation.
- The model refinery represents an average figure for refineries. Sampling model refineries gives no information about how individual refineries differ from this average.

In actuality, the only major variables that can be manipulated within the representative refinery concept are the size of the refinery (in terms of crude feedstock) and the process operating conditions (within the operating constraints of each individual process). For the purposes of developing quantitative and analytical data describing refinery solid waste streams, the single representative model refinery concept is clearly unsuitable. The inflexibility of sampling one or even a group of model refineries prevents detailed analyses of the different types of refineries, refinery process units, solid waste characteristics and quantities and refinery pollution control technology.

EPA/Refinery Classification and Proposed Model Refineries

One possible means of modeling the refining industry is to categorize the nation's petroleum refineries according to a logical set of basic characteristics, and to develop one typical representative model refinery for each of the categories. The total refining industry could then be simulated by sampling this group of model refineries. Solid waste generation rates and compositions representative of the entire industry could then be determined.

The EPA has developed refinery subcategories, shown in Table 3, which are reflective of the wastewater loading with respect to refinery type, processing units, and operating severity (EN-407). A representative model of each of the five refinery types could be developed and sampled as an average of all the refineries in each classification. The processing unit charge capacities and production capacities of each model refinery would correspond to the average capacities (expressed as a percent of total crude feed) of each of the various refinery types. It would be possible to simulate the process unit capacities and product output of the U.S. refining industry with selected groups of model refineries. An extensive amount of work would be required, however, to calibrate the sampling data obtained from the models such that they would best simulate the refineries within each category.

For example, it would be difficult to arbitrarily choose specific types of processing units and associated operating conditions that would accurately represent actual operations in the different types of refineries. It would be necessary to obtain from the refining companies a considerable amount of data concerning the operation of the individual processing units within the specific refineries. Companies are normally very reluctant to divulge this type of proprietary information.

TABLE 3

SUBCATEGORIZATION OF THE PETROLEUM REFINING INDUSTRY REFLECTING SIGNIFICANT DIFFERENCES IN WASTEWATER CHARACTERISTICS

Subcategory	Basic Refinery Operations Included
Topping	Topping and catalytic reforming whether or not the facility includes any other process in addition to topping and catalytic process. This subcategory is not applicable to facilities which include thermal processes (coking, visbreaking, etc.) or catalytic cracking.
Cracking	Topping and cracking, whether or not the facility includes any processes in addition to topping and cracking, unless specified in one of the subcategories listed below.
Petrochemical	Topping, cracking and petrochemical operations, whether or not the facility includes any process in addition to topping, cracking and petrochemical operations,* except lube oil manufacturing operations.
Lube	Topping, cracking and lube oil manufacturing processes, whether or not the facility includes any process in addition to topping, cracking and lube oil manufacturing processes, except petrochemical operations.*
Integrated	Topping, cracking, lube oil manufacturing processes, and petrochemical operations, whether or not the facility includes any processes in addition to topping, cracking, lube oil manufacturing processes and petrochemical operations.*

*The term "petrochemical operations" shall mean the production of second generation petrochemicals (i.e., alcohols, ketones, cumene, styrene, etc.) or first generation petrochemicals and isomerization products (i.e., BTX, olefins, cyclohexane, etc.) when 15 percent or more of refinery production is as first generation petrochemicals and isomerization products.

Source: EN-407.

In summary, sampling five model refineries instead of one would provide more flexibility and inherently greater accuracy in defining production rates and analytical characteristics of refinery solid waste streams. Still, an extensive base of refinery operating data would be needed to establish the validity of the model refinery samples as representative of the total industry.

Refinery Cluster Models

In some recent work done for the EPA, Arthur D. Little, Inc. (ADL), has defined the impact of several existing or proposed environmental regulations on the U.S. refining industry (LI-150, LI-151, LI-152). The development of a method for providing a detailed simulation of the U.S. refining industry constituted an important part of these studies. The acquisition and collation of an extensive refinery data base, which was used in calibrating the refinery models, was accomplished.

By sampling the ADL cluster model refineries, solid waste generation rates and analytical data from eighteen refineries could be used to accurately project generation rates and compositions of solid waste streams from the total U.S. refining industry.

Model Development

In the method developed by ADL, the refining industry, as it existed in 1973, was simulated by six individual refinery models. Each of the models, called "cluster" models, lies in a different geographical area of the U.S. and consists of a group of three existing operating refineries. In terms of crude oil type, process configurations, operating conditions, and product distributions, each group consists of refineries that are typical of the refining industry. Crude capacities of the model refineries ranged from 54,000 to 640,000 barrels/day; and each cluster model represented the average operation of the three refineries selected to comprise each group. Representatives of the EPA and members of a task force from the American Petroleum Institute (API) and the National Petroleum Refineries Association (NPRA) assisted ADL in the selection of the six geographical areas and the three refineries within each area.

The two most important criteria observed in the selection of representative regions and refineries were: (1) each selected cluster model was to represent, as nearly as possible, a typical and realistic refinery operation with respect to type, size of processing units, and operating flexibility; and (2) the crude slate, processing configuration, and product slates for each model were to be representative of the variations peculiar to each geographical region.

The six cluster models and the refineries comprising each cluster are listed in Table 4. The capacities of the refineries are shown for 1973, the calibration year, and as of 1 January 1976 and March 1978.

The Bureau of Mines has grouped refining operations into geographical refining districts which correspond with districts designated as PAD (Petroleum Administration for Defense) districts. These districts are briefly described in Table 5. The number of cluster models selected to characterize each PAD district reflects the refining capacity and the variations in the type of available crude found in each of the districts. For example, sufficient refining capacity and enough crude with common characteristics are available in PAD District I to permit characterization of that district with one cluster model, the East

TABLE 4

REFINERIES SIMULATED BY CLUSTER MODELS

PAD District	Cluster Identification	Refineries Simulated	1973 Capacity MBPCD	1976 Capacity MBPCD	1978 Capacity MBPCD
I	East Coast	Arco - Philadelphia, PA	160.0	185.0	185.0
		Sun Oil - Marcus Hook, PA	163.0	165.0	165.0
		Exxon - Linden, NJ	255.0	265.0	290.0
II	Large Midwest	Mobil - Joliet, IL	160.0	175.0	180.0
		Union - Lemont, IL	140.0	150.0	151.0
		Arco - East Chicago, IN	135.0	126.0	126.0
II	Small Mid-continent	Skelly - El Dorado, KS	67.0	78.7	81.0
		Gulf Oil - Toledo, OH	48.8	50.3	120.0
		Champlin - Enid, OK	48.0	53.8	54.0
III	Texas Gulf	Exxon - Baytown, TX	350.0	390.0	640.0
		Gulf Oil - Port Arthur, TX	312.1	312.1	335.0
		Mobil - Beaumont, TX	335.0	325.0	325.0
III	LA Gulf	Gulf Oil - Alliance, LA	174.0	180.4	196.0
		Shell Oil - Norco, LA	240.0	240.0	230.0
		Cities Service - Lake Charles, LA	240.0	268.0	268.0
V	West Coast	Mobil - Torrance, CA	123.5	123.5	123.0
		Arco - Carson, CA	165.0	181.5	180.0
		Chevron - El Segundo, CA	220.0	230.0	405.0

Source: LI-152.

TABLE 5

PAD DISTRICTS AND BUREAU OF MINES REFINING DISTRICTS

PAD District	Refining District
I	East Coast & Appalachian No. 1
II	Appalachian No. 2 & Indiana-Illinois-Kentucky & Oklahoma-Kansas-Missouri & Minnesota-Wisconsin-North Dakota-South Dakota
III	Texas Inland & Texas Gulf Coast & Louisiana Gulf Coast & North Louisiana-Arkansas & New Mexico
IV	Rocky Mountains
V	West Coast

Coast cluster. On the other hand, about 40 percent of the total U.S. refining capacity is contained in PAD District III. Two cluster models were used to simulate the refineries in this district because of its importance, and because two types of refinery configurations and crude slates were identified.

PAD District II, containing about 28 percent of domestic refining capacity, was also simulated with two refinery cluster models, since two distinctly characteristic types of refineries could be identified within the region. One was a large Midwest type refinery processing over 100,000 barrels/day of high sulfur crudes. The other type is typified by the small Midcontinent refinery in which 50,000-100,000 barrels/day of low sulfur crudes are refined.

PAD District V was characterized by a single refinery cluster model, the West Coast cluster. Since less than 5 percent of the country's refining capacity is located within PAD District IV (Rocky Mountains), it was not represented by a cluster model.

Four of the five EPA refinery types or categories (which are very similar to the five API refinery classes) are represented in the 18 refineries which make up the cluster models. The Type A (topping) refineries are not represented. Although there are 92 topping refineries in the U.S., they process only about 8 percent of the total crude. The omission of this type of refinery from the cluster models should not cause any problems in a solid waste study unless the Type A refineries are found to be sources of inordinate amounts of solid waste.

A summary of the major refinery processing units and capacities in each cluster model is presented in Table 6. These are compared with the average processing unit capacities

TABLE 6

SUMMARY OF MAJOR REFINERY PROCESSING UNITS FOR 1973

(Percentage of Crude Capacity)

Processing Unit	Texas Gulf Cluster	LA Gulf Cluster	PAD III Average	Large Midwest Cluster	Mid-Continent Cluster	PAD II Average	East Coast Cluster	PAD I Average	West Coast Cluster	PAD V Average
Catalytic Reforming	23	18	24	21	27	22	23	21	24	23
Catalytic Cracking	33	41	31	35	39	34	34	33	29	24
Hydrocracking	6	4	5	0	0	4	5	3	16	15
Alkylation	6	11	6	9	9	7	4	4	4	5
Delayed Coking	6	9	8	10	8	9	0	7	24	20

Source: LI-152.

(1973/1974) in refineries located within the same PAD districts as the cluster models. In general, the capacities of the cluster model(s) characterizing each PAD district agree with or bracket the average capacities of the respective PAD districts.

There are a few cases with an above-average deviation between the 1974 model values and the average district capacities. In PAD District I, the East Coast cluster contains no coking processes, even though coking capacity exists within the district. Coking operations were purposely omitted in order to have one cluster model without a coking unit, since many refineries do not carry out coking operations.

The capacities of the cluster model catalytic cracking units in PAD District II are higher than the average district capacities for this process. However, the cluster model refineries contain no hydrocracking units, so the composite of cracking operations compares well with the district average.

Utility of the ADL "Cluster" Model Refineries

The cluster model method defines eighteen refineries which would provide a valid sample base for simulation of the total U.S. refining industry. The advantage of sampling solid waste streams from the eighteen ADL cluster refineries over the two potential sampling programs discussed in Sections in the preceding sections are discussed below.

- The cluster models are based on individual existing and operating refineries. Thus, assumptions and conclusions based on work done with the models could be verified with existing data or through testing in these refineries.
- An extensive data base from these refineries and their operation already exists, and much of it has been gathered and evaluated by EPA and ADL.

- The methodology for calibrating these models and scaling them up has been developed. The procedures for altering or updating the models are available.
- The cluster models were developed in cooperation with API and industrial representatives. Thus, they should be familiar with this simulation method.
- From the results of scaling up these models, it appears that they are accurate in simulating the U.S. refining industry.
- Eighteen operating refineries were used in developing the cluster models. Eleven different companies are represented. Thus, a significant pool of existing refineries is identified.
- The refinery cluster models are all from different geographical areas of the country, but each represents a site of significant refinery operations. Environmental assessments based on the cluster models would be developed under different, yet realistic atmospheric conditions.
- Each of the cluster models has, as its feed, different composite crude oils. Thus, the effect of various crude oils on refinery operation and solid waste characteristics can be evaluated.
- The changing characteristics of the crude feedstock and the product slates have been projected through 1985. Future operating and solid waste characteristics can be evaluated if desired.
- The processing configurations of each of the refinery cluster models is different. Thus, the characteristics of many different processes can be evaluated while using only the six cluster models.

There are some deficiencies and omissions in the ADL cluster model simulation method.

- There are no topping refineries (EPA Type A refineries) represented in the clusters. There are over 90 of these refineries in the U.S. Most of them are small, however, and the total refining capacity of these refineries amounts to only 8 percent of the total U.S. capacity.

- Small refineries of less than 50,000 barrels/day capacity are not represented in the cluster models. Over half the refineries in the U.S. fall in this category. They refine only about one-quarter of the total U.S. refinery crude input, however.
- Production facilities for petrochemicals other than BTX are not included in any of the cluster models. If petrochemical manufacturing facilities are to be included within the scope of a planned study, they will either have to be incorporated into the existing models, or a new representative model or models will have to be developed.
- Prepration and execution of a detailed sampling program for eighteen refineries could be very expensive.

In order to determine whether the models as developed in 1974-75 are valid at the time of a planned study the current capacities of refineries and refinery process units should be compared to the base capacities. A recalibration of the models might be required if there are significant changes in capacity.

Refinement of Cluster Model Site Selection

The number of cluster models and the refineries selected by ADL to represent the five PAD classes reflect engineering judgement on: (1) what factors represent a typical and realistic refinery and (2) which crude slates, processing configuration and product slates for refineries selected within each model were typical of the variations peculiar to each PAD. The extent to which these model refineries agree with actual industry averages cannot be determined from the data collected for them. Therefore, no error limits or confidence intervals for the true generation factors can be derived.

Selection of refinery solid waste sample sites by the ADL approach could bias the data generated. Factors which control waste generation rates and characteristics have not been well defined. Even if the model refineries are well chosen, information gathered from sampling them would pertain only to the industry average. If guidelines were to be set at something other than the average, e.g., the 75th percentile, then the data collected from the model refineries would be of limited use. An alternative method can be utilized for developing a data base to be statistically analyzed.

The ADL approach does improve on the single representative refinery method by taking into account the different refinery configurations in setting up the PAD clusters. These clusters could serve as the basis for a stratified sampling approach to gathering the necessary information. Using this approach, each refinery would be classified into one of the six clusters and then a random sample from each of the classes would be drawn to determine the refineries to be sampled. This is a common method for increasing the precision of estimates made from survey data (see Hansen, Hurwitz and Madow).

Using this approach, poor selection of the clusters would only decrease the efficiency of the estimates made from the data and not result in an uncorrectable bias which would be the base with the model refinery approach. In addition, confidence intervals from the true average of all refineries and a characterization of the distribution of refineries around this average could be obtained.

APPENDIX V

SUPPLEMENTARY SAMPLING PROGRAMS

INTRODUCTION

This appendix addresses major areas to be addressed when conducting a refinery solid waste sampling program:

- Streams to be sampled
- Analytical methods
- Cost of sampling and analyses
- Sample collection guidelines

Streams

The major refinery solid waste streams, the number of samples required to characterize the stream and the phases to be analyzed are listed in Table 1. The individual constituents to be analyzed for are listed in Table 2.

Analytical Methods

The primary objective of the proposed analytical program is to determine whether potentially hazardous VOC constituents are present in refinery waste streams and to measure their levels of concentration. Determination of trace element contaminants of the waste streams is a second objective. Applicable methods for analyses of the various constituents and rough cost estimates are listed in Table 3.

Cost Comparisons

Using the PAD refinery classes the population of refineries can be stratified into six categories. A random sample

TABLE 1

SOLID WASTE STREAMS
NUMBER OF SAMPLES AND PHASES TO BE ANALYZED

	Number of Analyses Per Refinery		
	Hydrocarbon Phase	Aqueous Phase	Solid Phase
Refinery Background Samples			
Intake Waters	---	2	2
Background Soil	---	---	3
Crude Oil	3	---	3
Solid Wastes Samples			
Once-Through Cooling Water Sludge	---	---	1
Cooling Tower Sludges	---	---	2
Alkylation Sludge	---	1	1
Waste FCC Catalyst	---	---	1
Treating Clays	2	---	2
Tank Bottoms	4	4	4
Storm Water Silt	---	---	1
API Separator Bottoms	2	2	2
Air Flotation Float	2	2	2
Waste Biological Solids	1	1	1
Slop Oil Emulsion Solids	2	2	2
Exchanger Bundle Cleaning Solids	1	1	1
Coke Fines	---	1	1
Boiler Feedwater Lime Sludge	---	---	1
Treatment Residue Samples			
Sludge Dewatering	2	---	2
Sludge Farming	2	2	2
Incineration	2	2	2
Total	23	20	36

TABLE 2

REFINERY SOLID WASTE CONSTITUENTS TO BE ANALYZED

Hydrocarbon Phase

- Arsenic
- Benzene
- Benzo-a-pyrene
- Cadmium
- Chromium (Total)
- Copper
- Cyanide
- Fluoride
- Lead
- Mercury
- Nickel
- Phenol
- PNA (Priority)
- Selenium
- TOC-VOC
- Vanadium
- Zinc

Aqueous Phase

- Arsenic
- Benzene
- Benzo-a-pyrene
- Cadmium
- Chromium (Total)
- Chromium (Hexavalent)
- Copper
- Cyanide
- Fluoride
- Lead
- Mercury
- Nickel
- Phenol
- PNA (Priority)
- Selenium
- TOC-VOC
- Vanadium
- Zinc

Solid Phase

- Arsenic
- Benzene
- Benzo-a-pyrene
- Cadmium
- Chromium (Total)
- Copper
- Cyanide
- Fluoride
- Lead
- Mercury
- Nickel
- Phenol
- PNA (Priority)
- Selenium
- TOC-VOC
- Vanadium
- Zinc

Total Sample

Phase Portions

- Hydrocarbon Phase %
- Aqueous Phase %
- Solid Phase %
- Loss %

TABLE 3

REFINERY SOLID WASTE STREAM ANALYSES
CURRENTLY USED METHODS AND COSTS

Analysis	Method	Cost Per Sample ($)
Arsenic	AA-Graphite Furnace	30
Benzene	Gas Chromatography/Mass Spectrometry	300
Benzo-a-pyrene	Gas Chromatography/Mass Spectrometry	150*
Cadmium	AA-Graphite Furnace	30
Chromium (Total)	AA-Graphite Furnace	30
Chromium (Hexavalent)	AA-Flame	40
Copper	AA-Graphite Furnace	50
Cyanide	Distillation, Colorimetry	50
Fluoride	Specific Ion Electrode	20
Lead	AA-Graphite Furnace	50
Mercury	AA-Cold Vapor	50
Nickel	AA-Graphite Furnace	40
Phenol	Distillation, Colorimetry	67
PNA (Priority)	Gas Chromatography/Mass Spectrometry	100**
Selenium	AA-Graphite Furnace	40
TOC	Non-Dispersive Infrared Analysis	40
Vanadium	AA-Graphite Furnace	45
VOC	Purge/Trap-GC	100***
Zinc	AA-Graphite Furnace	40

---

*BAP only.

**In addition to BAP.

***Estimated.

could be selected from each category to form the total sample. If the categories actually do have different average generation rates, then a more precise estimate of the population mean will be obtained than with a simple random sample. Even if the categories do not have different average generation rates, an unbiased estimate of the population mean can still be obtained using the stratified sample.

The number of refineries to be sampled from each category depends on the resources available and the precision with which it is desired to estimate the population generation factor.

After consulting with refinery personnel and Radian engineers experienced in refinery sampling projects, sampling plans for selecting 50, 80 and 110 samples from a refinery were developed and are contained in Table 4. Cost estimates for the three sample plans for 6, 12, 24 and 36 refineries were made and are contained in Table 4.

In order to select a sampling plan i.e., the number of refineries to be sampled and the number of samples per refinery, information is needed on how well the population generation factor is estimated using a particular plan. The variance of a sample for a particular stream taken from a randomly chosen refinery is:

$$\sigma^2 = \sigma^2{}_B + \sigma_W{}^2$$

where: σ^2 is the total variance of the sample

$\sigma^2{}_B$ is the component of the variance due to differences between refineries.

$\sigma_W{}^2$ is the component of variance associated with the stream variation within the refinery.

TABLE 4

SOLID WASTE SAMPLING AND ANALYSIS COMPARISON PRECISION VS. COST

Number of Refineries	Samples Per Refinery	[1](σ/GF)x100%	[2](σ/GF)x100%	Cost ($M̄)
6	50	72.4	72.4	.54
6	80	69.3	66.1	.82
6	110	66.1	59.1	1.13
12	50	51.2	51.2	1.08
12	80	49	46.7	1.69
12	110	46.7	41.8	2.18
24	50	36.2	36.2	2.19
24	80	34.7	33.0	3.31
24	110	33.0	29.6	4.65
36	50	29.6	29.6	3.20
36	80	28.3	27.0	4.93
36	110	27.0	24.1	6.85

---

[1] $\sigma^2_B = 2\sigma_W^2$

[2] $\sigma^2_B = \sigma_W^2$

Using the relative magnitudes of σ^2_B and $\sigma_W{}^2$ the proper balance between the number of refineries and the number of samples per refinery can be established. For example if σ^2_B is large compared to $\sigma_W{}^2$ than it is more efficient to place emphasis on visting a large number of refineries rather than sample extensively from a few refineries.

If N refineries are sampled and n samples selected for a particular stream, then the variance of the generation factor is:

$$\sigma_{GF}{}^2 = \frac{\sigma^2{}_B}{N} + \frac{\sigma_W{}^2}{Nn}$$

This assumes no gain in precision from the stratification of the population. If the categories do have different generation rates then the variance of the generation rate will be smaller than that given by the equation above. For purposes of this analysis precision will be described by the coefficient of variation, (σ_{GF}/GF) x 100% that is, the standard deviation of the generation factor expressed as a percent of the generation factor.

Since all refineries in the OAQPS study reported generating solid wastes from the API separator and since the generation factor for this stream and its associated variance were typical of other high generating streams, this stream was chosen as a basis for the cost comparisons. In this study the generation factor for API separator sludge was estimated to be 3.19 metric tons/year per 1000 barrels/stream day; and its variance was 32. It was assumed that within refinery variation $\sigma_W{}^2$ in this study was comparable to that which would be obtained from 50 samples. Using these values the precision of each of the 12 sampling plans considered was calculated for two cases $\sigma^2{}_B = 2\sigma_W{}^2$ and $\sigma^2{}_B = \sigma_W{}^2$. These values along with the costs are given in Table 4.

One conclusion which is obvious from looking at Table 4 is that the plans calling for 110 samples per refinery are not economical. At least for the two cases considered a plan with 50 samples can be found which has better precision and costs the same or less. For example, considering the case $\sigma^2_B = 2\sigma_W^2$, the plan calling for 12 refineries and 110 samples per refinery has precision 46.7 and costs \$2.18m while the plan with 24 refineries and 50 samples has precision 36.2 and costs approximately the same, \$2.19m.

The coefficients of variation can be related to how well the generation factor will be estimated for a particular plan. The largest discrepancy between the estimated and true generation factor which could reasonably be expected is approximately twice the entry in the table. For example, considering the case $\sigma^2_B = \sigma_W^2$ and the plan of 12 refineries and 80 samples, the estimated generation factor could reasonably be expected to be within 93.4% of the true generation factor.

Sample Collection

The following guidelines were developed after reviewing the sample collection procedures utilized by the API and Jacobs Engineering. Also, refinery personnel involved in the previous sampling programs were contacted to discuss problems associated with obtaining representative refinery waste samples.

1. Many of the samples required for this proposed survey have three distinct phases (hydrocarbon, aqueous, and solid). While obtaining the sample, care should be taken to preserve the ratio of the three phases in the sample taken.

2. Samples should be collected in sufficient volume to minimize sampling errors and to provide enough sample for analytical aliquots to be supplied to two or more laboratories. Four-fifths of a gallon in a new, clean one-gallon can is suggested

for most of the samples. Samples from tank or vacuum trucks should be no less than four gallons in a five-gallon crimped top pail to be representative.

3. Plastic sample containers should not be used for field samples.

4. As a minimum, samples should be labeled to include the following information:

- Date
- Refinery
- Unit
- Person sampling
- Identification number
- Any special sampling conditions.

5. The discharge from sludge removal or conveyance pumps, such as the pumps for the bottoms in an API separator or for the float in an air flotation unit, should be sampled as any refinery flowing stream would be sampled.

6. Wastes should be sampled as near as possible to the points of origin in the refinery, and care should be taken to prevent evaporation of volatiles from the sample. For some streams, additional samples may be desired after transportation, dewatering, etc.

7. In the case of liquid or semi-solid wastes, numerous small grab samples taken over a period of time will yield a more representative sample.

8. Field samples should be separated on the day collected into equivalent analytical aliquots. The field sample should be made a homogeneous as possible by the use of a paint shaker, if available, or by vigorous stirring. Aliquots should be stored in glass. These aliquots should be refrigerated until the analyses are complete.

9. On each sample date, refinery personnel assisting in the sampling should be consulted to ensure that the particular process is running normally and that the waste is as representative as possible.

Phase data summarized in Table 4-1 may assist the sampling team in determining the tools and procedures required for obtaining representative samples.